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Professor of Chemistry, University of Allahabad; President, Section of Chemistry, 57th Indian Science Congress, 1970; General Secretary, Indian Science Congress Association, 1980-83; Vice-President, Indian Chemical Society, 1980 & 1981; Acharya P. C. Ray Memorial Awardee

PREFACE

On the occasion of his sixtieth birthday, the former students, colleagues and associates in research of Professor Arun K Dey felicitated him on 20th October 1982 in a function organised in the Vizianagaram Hall of the University of Allahabad. Professor U. N. Singh, Vice-Chancellor of the University presided and Professor S Ghosh, former Head of the Department of Chemistry, Universities of Allahabad and Jabalpur, was the Chief Guest. A souvenir volume was presented to Professor Dey on behalf of the Felicitation Committee by Professor R. C. Kapoor of Jodhpur University. The Felicitation Committee is indebted to the Council of the Indian Chemical Society for dedicating this issue of the Journal of the Indian Chemical Society to Professor Arun K Dey as a tribute to his services to the cause of Chemistry and Science Education in the country.

This special number of the journal contains invited articles from distinguished workers from various countries, and we are sincerely thankful to the authors for responding favourably to our invitation. We are grateful to Professor S Ghosh, Professor R D Tiwari and Professor H. L Nigam for their kindness in going through the manuscripts

The Felicitation Committee deeply appreciate the active interest taken by Professor S K. Talapatra, Honorary Secretary and the cooperation received from Dr. S. K. Roy, Executive Editor.

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Synthesis of Sulphur and Nitrogen Heterocyclics Involving Rearrangement *Via* Small Rings*

B. D. TILAK

Indian Institute of Education, Pune-411 029

IT is indeed a great honour to be called upon to deliver the Acharya Prafulla Chandra Ray Memorial Lecture (1978). I am grateful to the Indian Chemical Society for conferring on me this distinction.

Acharya Ray not only founded the Indian Chemical Society but was also the father of Indian Chemistry and Chemical Industry. I pay my humble homage to this great man to whom the nation owes so much.

In this lecture, I wish to briefly cover my work over the last twenty years, pertaining to the synthesis of sulphur and nitrogen heterocyclics, wherein we came across rearrangements which could be rationally explained by postulating the involvement of small (three or four membered) sulphur and nitrogen ring systems. In a few cases compounds representing these small ring systems were also isolated or synthesised and then isomerized to five and six membered heterocyclics in a two step sequence.

X = –S–, –NH–

X_1^+ = –S^+=, –N=

ClO_4^-

R_1, R_2 = Alkyl/Aryl groups

Chart 1

The general method of synthesis of sulphur and nitrogen heterocyclics involved cyclodehydration of suitably substituted ketones or carbinols where the carbonyl and hydroxyl groups involved in the cyclodehydration reaction were removed from the hetero atom by one or two carbon atoms (*via* a methylene, dimethylene group or a double bond). The end products were the expected cyclodehydration products as well as the rearrangement products where the substituents attached to the carbonyl/hydroxyl group carrying carbon atoms and those attached to the carbon atoms linked directly to the hetero atom in the aliphatic chain were found to be interchanged. The general scheme of these reactions is shown in Chart 1. Synthesis of other sulphur/nitrogen heterocyclics arising out of the general schemes shown in Chart 1 are also described.

Synthesis of 5-membered sulphur heterocyclics via thiiranium salts :

Cyclodehydration of phenacyl phenyl sulphide 1 and its derivatives, (by treatment with PPA) was reported earlier[1] to give mostly 2-phenylthionaphthene 2. We however showed that the reaction gave both the 2-phenyl 2 (47%) as well as 3-phenylthionaphthene 3 (15%)[2]. Earlier reports[1] on cyclodehydration of phenacyl *p*-toluyl sulphide 4

1, R=H
4 R=CH_3

3, R=H
5, R=CH_3

2, R=H
6, R=CH_3

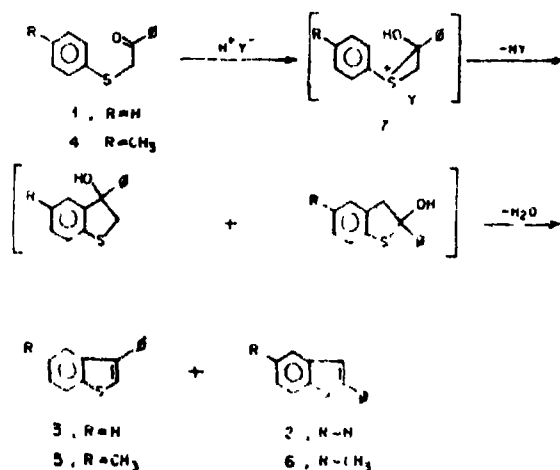
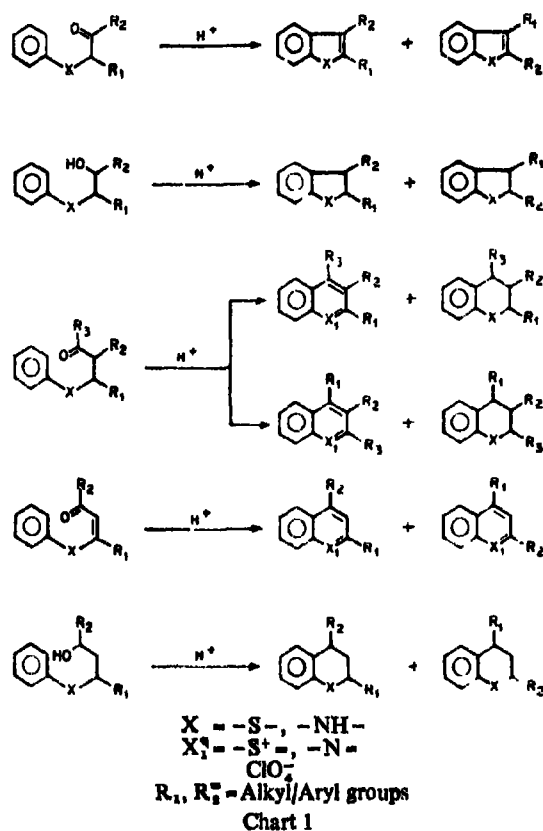



CHART 2

* Acharya Prafulla Chandra Ray Memorial Lecture (1978) delivered under the auspices of the Indian Chemical Society at Pune on 21st December, 1981.

were likewise revised by us[8] to show that the reaction gave both the expected 5-methyl-3-phenylthionaphthene 5 (25%) as well as the rearranged 5-methyl-2-phenylthionaphthene 6 (36%). The formation of the rearranged cyclodehydration products 2 and 6 in the above reactions was explained by us by postulating the intermediate formation of the three-membered sulphur heterocyclic intermediate, a thiiranium salt 7 which then ring expands in two alternative ways to yield the two sets of thionaphthenes 3, 5, (normal products) and 2, 6, (rearranged products)[8] (Chart 2).

Similarly, cyclodehydration of 2-thionaphthacyl phenyl sulphide 8 with P_2O_5 or PPA gave both the normal cyclodehydration product 2,3'-dithionaphthenyl 9 as well as 2,2'-dithionaphthenyl 10[8] which probably arises by rearrangement *via* the relevant thiiranium salt reactive intermediate 11 (Chart 3).

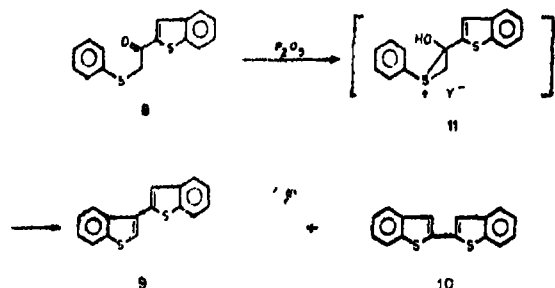
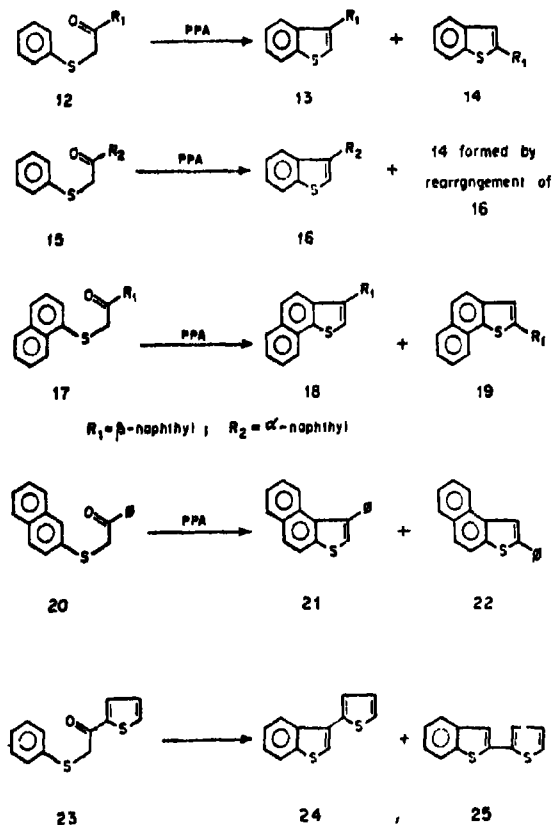



Chart 3

Several more such rearrangements were also reported by us during the cyclodehydration of other aroylmethyl aryl sulphides[4,8]. Most of them led to two sets of arylthionaphthenes, one the normally expected cyclodehydration product and the other the rearrangement product (Chart 4). These rearrangements could also be explained on the basis of involvement of reactive thiiranium salts as reactive intermediates.

14 formed by rearrangement of 16

R_1 = β-naphthyl ; R_2 = α-naphthyl

Chart 4

It is interesting to note that cyclodehydration of α-phenylmercaptopropiophenone 26 with PPA gave only the normally expected 3-phenyl-2-methylthionaphthene 27 and the rearranged product 2-phenyl-3-methylthionaphthene 28 could not be traced[4]. However, in the light of more sophisticated techniques of analysis and separation now available it is desirable to re-examine these results (Chart 5).

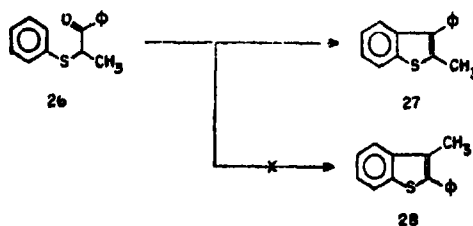



Chart 5

The above rearrangements, observed during cyclodehydration of aroylmethyl aryl sulphides, have also been found to occur in the acid catalysed cyclodehydration of aroylmethyl aryl ethers and aroylmethylarylamines (or secondary amines) 29 where also both the normally expected benzofurans and indoles 30 and the rearranged cyclodehydration products 31 are formed[6,7] (Chart 6). Several other rearrangement reactions in the synthesis of benzo-*b*-thiophenes during acid-catalysed cyclodehydrations of relevant keto-sulphides are also reported[8]. All these rearrangements probably occur through three-membered sulphur 7, oxygen (32, $X_1 = -\overset{+}{O}=$) and nitrogen (32, $X_1 = -\overset{+}{N}=$) heterocyclic rings (Charts 2, 6).

X = -O- , R-N<

X_1 = $-\overset{+}{O}<$, $R-\overset{+}{N}<$; Y^-

R = H , alkyl

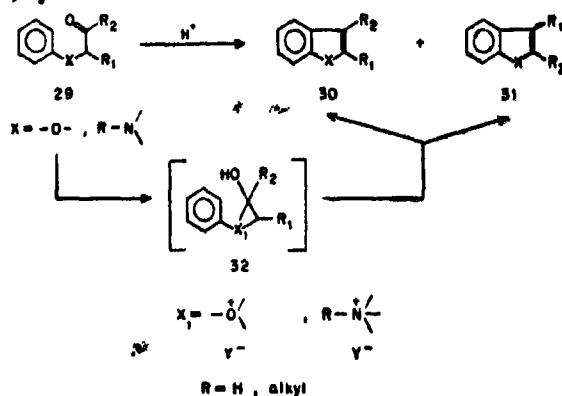



Chart 6

The involvement of a thiiranium salt 33 and N,N-dialkylaziridinium salt 34 is widely recognized in explaining the biological activity (as alkylating agents) of mustard gas and nitrogen mustards. We had also suggested the possible involvement of

thiiranium salts 35 and 36 to account for the carcinostatic activity found by us for thiodiglycol and thiodiglycollic acid[9] (Chart 7).

$S(CH_2CH_2Cl)_2$ ⟶ 33

$H_3C{-}N(CH_2CH_2Cl)_2$ ⟶ 34

$S(CH_2CH_2OH)_2$ ⟶ 35

$S(CH_2CO_2H)_2$ ⟶ 36

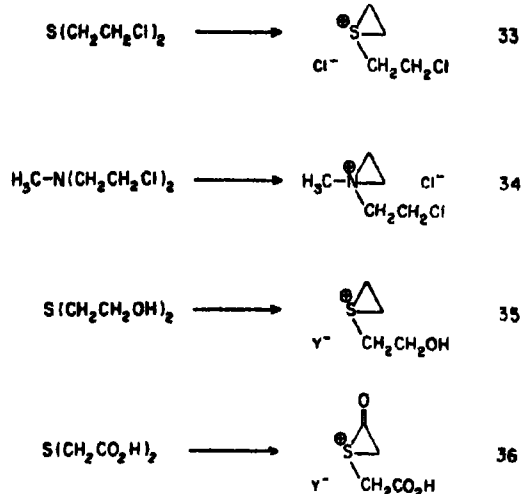



Chart 7

Acid catalysed cyclodehydration of β-hydroxylalkyl aryl sulphides 37 also gave both the normal 2,3-dihydrobenzo-*b*-thiophenes 38 as well as the rearranged thiophenes 39. Here also the rearrangement products are obviously formed *via* the reactive intermediate S-arylthiiranium salts 40 (Chart 8). In a few cases these reactive intermediates 40 were also isolated and then isomerized to the two sets of products 38 and 39[10,11]. The ratios of the normal and rearranged 2,3-dihydro-benzo-*b*-thiophenes and the proportion of *cis-trans* isomers obtained are also shown in Chart 8.

37	38 Cis / trans (%)	39 Cis / trans (%)
$R_1 = \Phi$, $R_2 = H$	45	55
$R_1 = \Phi$, $R_2 = CH_3$	52 (32 20)	48 (30 18)
$R_1 = R_2 = \Phi$	← 100 →	
$R_1 = CH_3$, $R_2 = \Phi$	18 (12 6)	82 (73 9)
$R_1 = CH_3$, $R_2 = H$	50	50

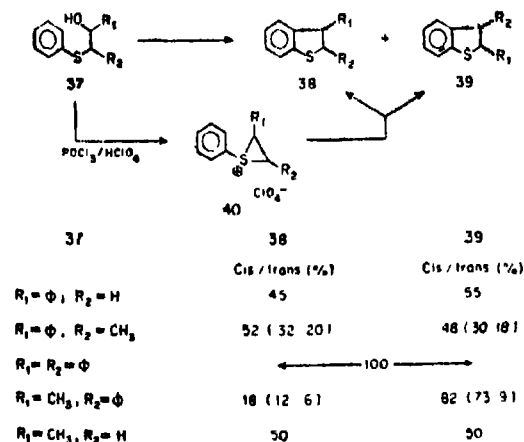



Chart 8

Synthesis of sulphur heterocyclics containing bridge-head sulphonium salt moiety :

Apart from the above thiiranium salts, we have also synthesised several five- and six-membered heterocyclic sulphonium salts, in some of which heterocyclic sulphur occupies a bridge-head position[12-15]. The synthesis of some of these sulphur and nitrogen heterocyclics involves rearrangement of incipient carbonium ions by 1,2-alkyl or proton shifts[12-14] (Chart 9).

$Y^- = ClO_4^-$, I_3^-, Bi^-; $n = 1,2$; $X = {>}C{-}H$, ${-}N{<}$ (48)

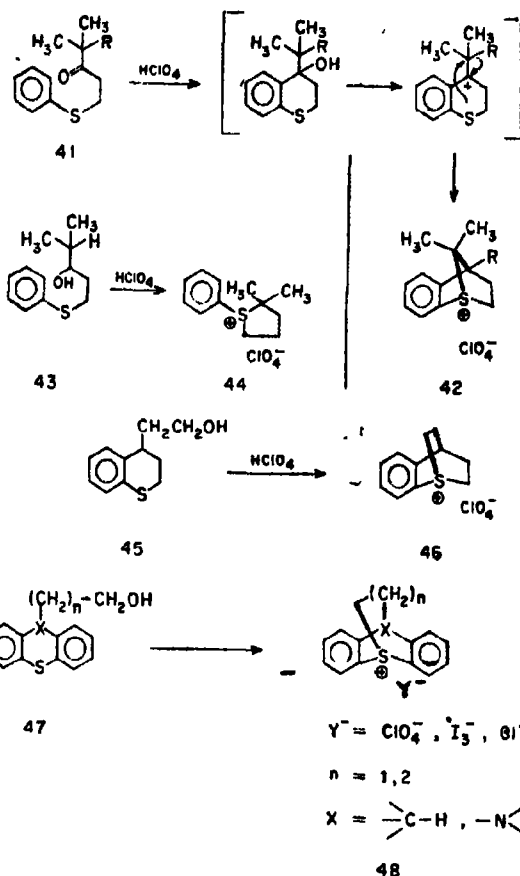



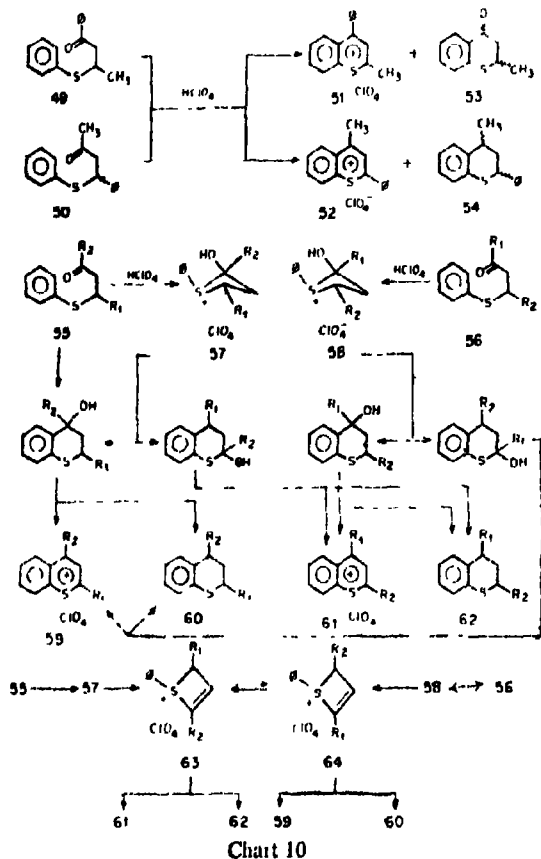
Chart 9

Synthesis of six-membered sulphur heterocycles via S-arylthiacyclobutanium and S-arylthiacyclobutenium salts :

Rearrangement reactions occuring through reactive three-membered heterocyclic intermediates described above were also observed during the synthesis of six-membered sulphur and nitrogen heterocyclic compounds through acid-catalysed cyclodehydration of appropriately substituted ketones and carbinols. Here also the rearrangement most probably occurs through reactive four-membered sulphur and nitrogen heterocyclic ring systems which then ring expand in two alternative ways to give the observed products. In several cases the relevant reactive four-membered sulphur and nitrogen heterocyclic compounds were also isolated and then isomerized to six-membered ring systems, the observed products of cyclodehydration reactions.

Thus, cyclodehydration of both β-phenylmercaptopropyl phenyl ketone 49 and β-phenyl-β-phenylmercaptoethyl methyl ketone 50 gave a mixture of two sets of thianaphthalenium salts 51 and 52 and the thiachromans 53 and 54 in different proportions. The fact that *all* the four compounds are obtained starting from two *different* starting β-arylmercaptoethyl ketones, 49 and 50, goes to show that the cyclodehydration probably occurs through four-membered saturated (S-phenylthiacyclobutanium

salts) 57, 58 or unsaturated (S-phenylthiacyclobutenium salts) 63, 64 sulphur ring systems as shown in the generalized scheme in Chart 10. The hydroxycyclobutanium salts 57, 58 are obviously unstable and readily yield S-phenylcyclobutenium salts 63, 64 which were isolated in several cases and then isomerized to the six-membered sulphur ring systems, the observed products of cyclodehydration of the β-arylmercaptoethyl ketones. Depending on the nature of substituents (R_1, R_2), 63 or 64 are more stable (in acidic solutions) and the less stable compound is slowly converted to the more stable thiacyclobutenium salt[16-18]. Consequently, the relative proportion of the normal as against the rearranged products in the above cyclodehydration reactions will depend on the nature of substituents R_1 and R_2 and the relative stability of the incipient carbonium ions involved in the cyclization step.

Chart 10

Proton abstraction from the yellow coloured thiacyclobutenium salts, 63 and 64, by treatment with sodium hydride, gave an identical olive green coloured neutral compound which is assigned a ylid (in preference to thiacyclobutadiene) structure as shown in Chart 10A. Reprotonation of the ylid yields the more stable of the two thiacyclobutenium salt 63 or 64[17]. Whereas these ylids could not be isolated and were unstable, several stable neutral sulphur heterocyclics, containing S(IV) atom, were prepared by us rather simply by thionation of appropriately substituted 1,8-dichloroanthraquinones and 1,4,5,8-tetrachloroanthraquinone. These are deeply coloured (red to green) quinonoid compounds some of which are used commercially as vat dyes for cotton[84] (Chart 10A).

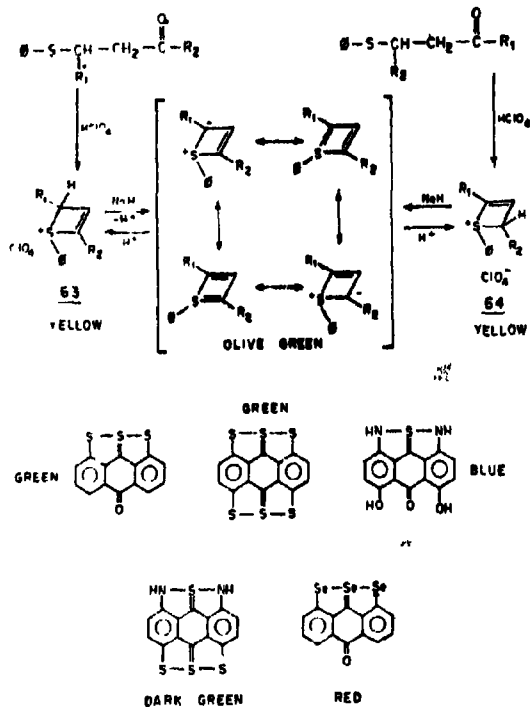



Chart 10A

Cyclodehydration of β-arylmercaptomethylene ketones 65 by means of perchloric acid gave

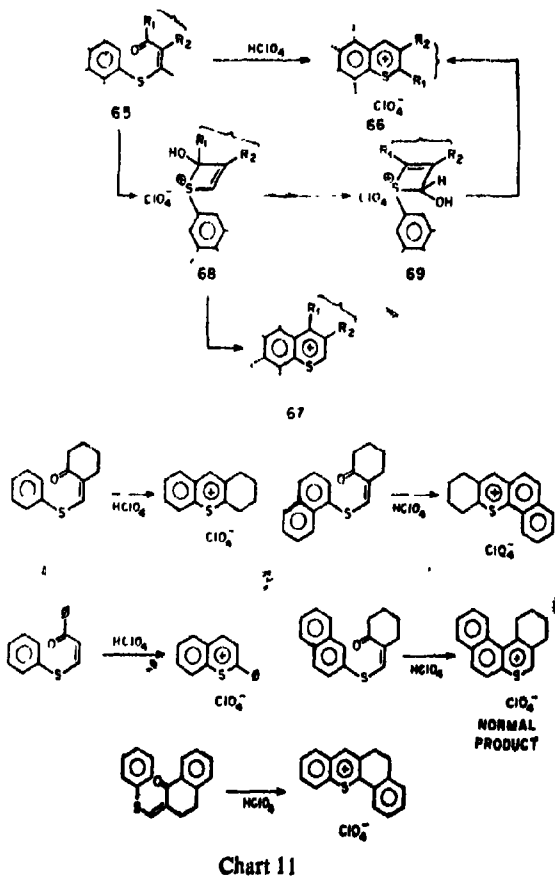



Chart 11

essentially the rearranged thianapthalenium perchlorate 66 and only smaller amounts of the normal product 67. It seems likely that the rearranged products are formed through the intermediacy of reactive hydroxythiacyclobutenium perchlorates, 68, 69, which then lead to observed products 66, 67 (Chart 11)[19]. Several complex linear and angular polycyclic thianapthalenium perchlorates were synthesised by this general method. In most cases cyclodehydration of the β-arylmercaptomethylene ketones gave only the rearranged thianapthalenium perchlorates (Chart 11)[19].

Cyclodehydration of 1-phenyl-1-phenylmercaptoethyl-3-butanol 71, obtained by $NaBH_4$ reduction of β-phenyl-β-phenylmercaptoethyl methyl ketone 70, by treatment with perchloric acid yields mostly the rearranged 2-methyl-4-phenylthiachroman[18] 72. The formation of the latter rearranged product is also explicable on the basis of intermediate involvement of 1-S-phenyl-1-thiocyclobutanium salt 73 (Chart 12). However, attempts to synthesise the latter compounds have not been successful so far.

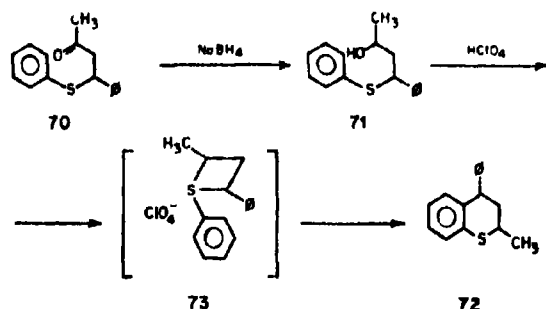



Chart 12

Synthesis of quinolines via *azetidines and azetines* :

In analogy with the above acid catalysed cyclodehydration reactions, 1-arylamino-3-alkanols 74 gave both the normal 75 as well as the rearranged 76 tetrahydroquinolines[20,21]. The formation of the rearranged tetrahydroquinolines 76 is explicable by postulating the intermediate involvement of N-arylazetidines 77 which on ring expansion lead to 75 and/or 76 depending on the nature of substituents and their stereochemistry[18]. The relevant N-arylazetidines were also synthesised from the corresponding carbinols 74 by cyclodehydration with sulphuric acid[22] or better with triphenylphosphine dibromide in presence of triethylamine[23]. Stereospecific synthesis of the azetidines and their stereo-selective conversion to *cis*- or *trans*-tetrahydroquinolines has also been achieved[18] (Chart 13).

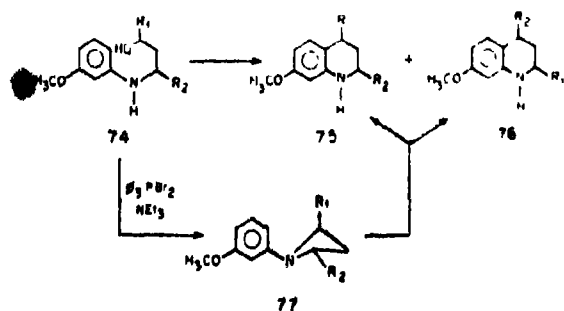



Chart 13

Cyclodehydration of β-arylaminoethyl alkyl/cycloalkyl/aryl ketones 78 by treatment with fused zinc chloride and an arylamine hydrochloride in boiling ethanol gave a mixture of rearranged quinolines 79 and tetrahydroquinolines 80 alongwith the normal cyclodehydration products 81, 82. The formation of rearranged products is explicable by envisaging the intermediate formation of N-arylazetidines 83 or through the involvement of N-arylazetines[18,24,25,26] 84, 85 as shown in Chart 14.

L = -NH-aryl, OH, -O-ZnCl

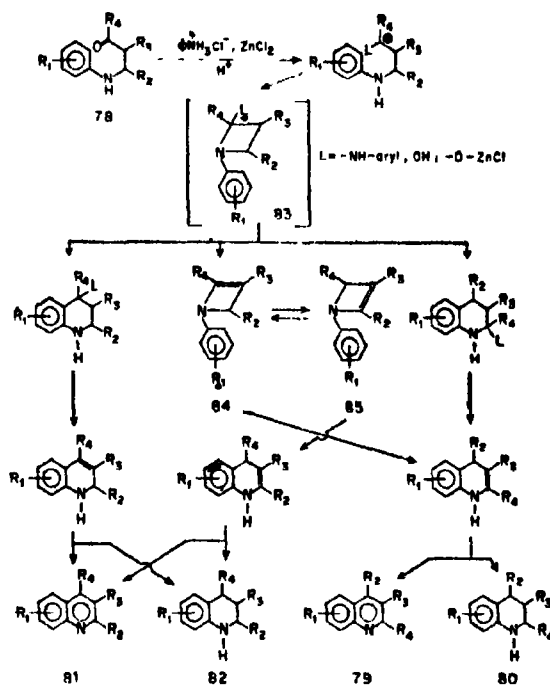



Chart 14

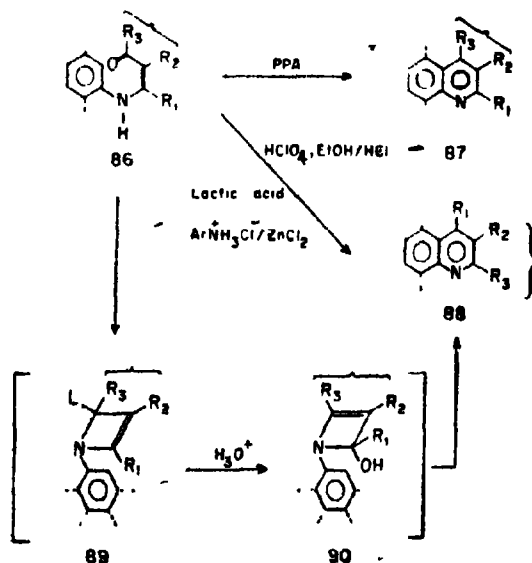
Cyclodehydration of β-arylaminomethylene aryl

L = Leaving group e.g. $ArNH_2$, OH, – Lactate, –O–ZnCl

Chart 15

ketones 86 by treatment with PPA gave in most cases the relevant quinolines[26] 87, whereas treatment of 86 with arylamine hydrochloride and fused zinc chloride in boiling ethanol, chloroacetic acid, lactic acid, ethanolic hydrochloric acid or perchloric acid gave the rearranged quinolines 88. The rearrangement may be taking place through reactive intermediate azetines 89, 90 (Chart 15) although other plausible mechanisms have also been suggested[85]. A large number of quinolines of the general formulae 87, 88 have been synthesised by us[26,86] (Chart 16). Attempts to isolate or to synthesise N-arylazetines of the type 89, 90, however, proved unsuccessful. There is also no report in literature of the synthesis of N-arylazetines.

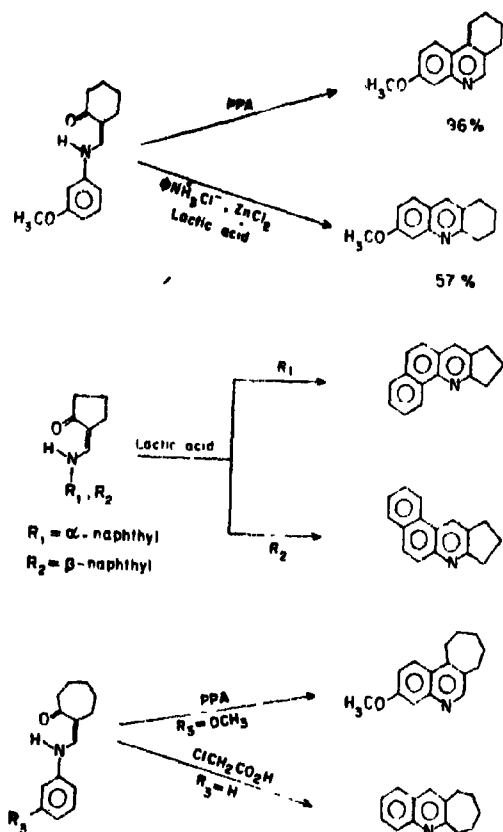



Chart 16

Several complex sulphur and nitrogen containing heterocyclic compounds were also synthesised by cyclodehydration of the relevant β-arylaminomethylene ketones where also the heterocyclics were obtained through rearrangement, possibly through the relevant azetines[87-91]. Some of these syntheses are shown in Chart 17 by way of illustration.

Chart 17

Synthesis of 3,4-dihydro-1,3,2-oxazaphosphorin-2-oxides and their rearrangement to quinolines :

In view of the synthesis of S-arylcyclobutenium perchlorates by interaction of β-arylmercaptoethyl alkyl (aryl) ketones with $POCl_3/HClO_4$ discussed earlier, β-arylaminoethyl aryl ketones 91 were treated with $POCl_3$ and later (or simultaneously) with triethylamine. Instead of the expected azetines, 92

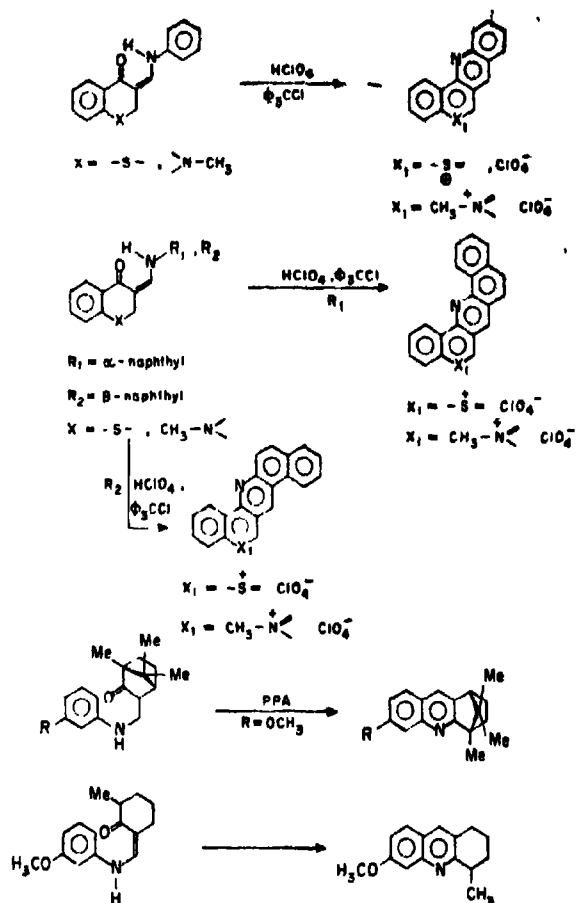
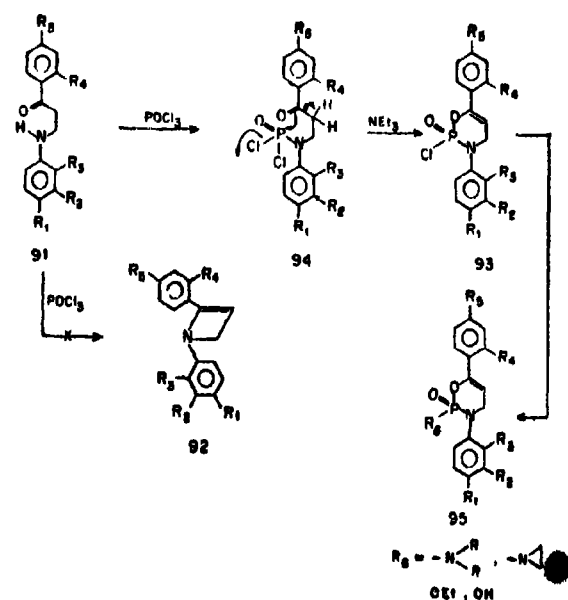



Chart 18

2-chloro-3, 6-diaryl-3, 4-dihydro-1, 3, 2-oxazaphosphorin-2-oxides **93** were formed readily through intermediate phosphoramides **94**, which were also isolated in a few cases (Chart 18). Four compounds in this series **93** were found to be active against P388 lymphocytic leukemia[82]. Whereas tetrahydro-1,3,2-oxazaphosphorin-2-oxides (cyclophosphamides) are widely studied and some of them (e.g, Endoxan) are well known and widely used anti-leukemic agents, the 3,4-dihydro-1,3,2-oxazaphosphorin-2-oxides **93** represent new O,N,P, heterocyclic ring system. These compounds are very stable to heat, light, hydrolytic cleavage and dilute acids and alkali. The chlorine atom in **93** is, however, replaced by secondary alkylamino, azido, ethoxy and hydroxy (in the presence of phase transfer catalysts) groups to give 2-substituted-3,6-diaryl-3,4-dihydro-1,3,2-oxazaphosphorin-2-oxides **95**.

The oxazaphosphorin **96** was slowly converted on keeping to 7-methoxy-4-phenylquinoline **97** in high yield (90%). The transformation was rapid on photolysis, acid treatment or heating in benzene with or without Et_3N. Some 7-methoxy-4-phenyl-1,2,3,4-tetrahydroquinoline **98** (yield 6%) was also formed. This transformation seems to be specific for **96** since other oxazaphosphorins **93**, **95** failed to give the corresponding quinoline derivatives (Chart 18). The mechanism of this facile conversion of **96** to **97** in high yield, even in *absence* of air, is under investigation.

Synthesis of azepines through nitrene insertion :

Thermal decomposition of *p*-toluenesulphonylazide **99** with benzenoid substrates containing electronegative substituents such as carbomethoxy, nitro, cyano, acetyl, dicarbomethoxy or dicarboethoxy groups yielded the azepines **104** and *p*-toluenesulphonamido dreivatives **103**, of which the former are formed in greater (*albiet* low) yield[83,84]. The formation of azepines involves the addition of thermally generated (singlet) nitrene **100** across the double bond carrying the electro-negative substituent. Ring expansion of the resulting unstable aziridines **102** then yields the relevant azepines **104** (Chart 19).

$R_1 = CO_2Me, R_2 = H$, $R_1 = R_2 = CO_2Me, CO_2Et$
$R_1 = COCH_3, R_2 = H$, $R_1 = NO_2, R_2 = H$
$R_1 = CN, R_2 = H$

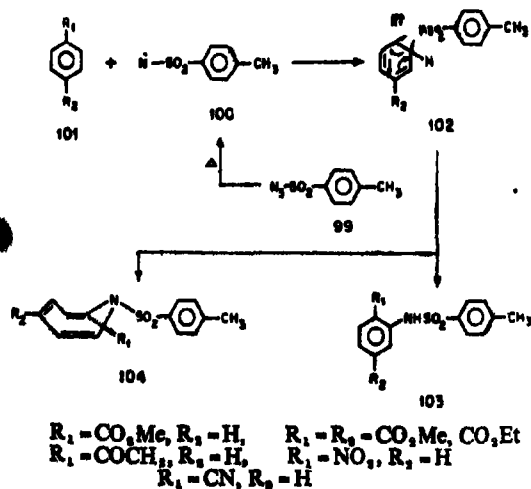



Chart 19

Thermal interaction of **99** with dimethyl phthalate and anthraquinone gave the azepines **105** and **106** and 1-*p*-toluenesulphonamidoanthraquinone **107**[85] (Chart 20).

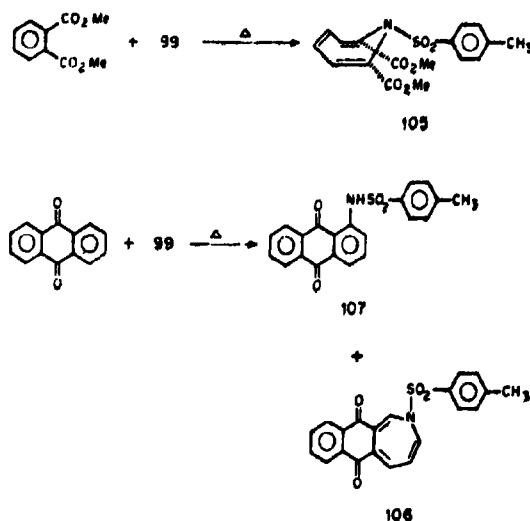



Chart 20

Although the yield of the above azepines were generally very low (5-20%), in view of the inaccessibility of these complex azepines by other methods, the present work may be of some interest.

Acknowledgement

The author records his thanks to his numerous research students and collaborators (listed in the references) but for whose dedication, devotion, hard and skilful work the above contributions, spread over the last twenty years, would not have been possible.

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FIR Studies of Copper(II) Monohaloacetates : Molecular Structure Based on Cu-O Vibrations

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FIR studies of copper(II) acetate monohydrate, fluoroacetate dihydrate, chloroacetate tetrahydrate and bromoacetate monohydrate have been made in crystalline state at room temperature and at low temperature. The number of Cu-O bands, active in ir, have been calculated theoretically for different possible moieties around Cu atom in the complexes and compared with the total number of bands actually observed in the spectra. A tentative assignment of Cu-O bands have been proposed. On the basis of shifting of Cu-O stretching bands, bridged cage type mode of coordination of the carboxylate ligand to the Cu atom and dimeric bridged cage structure of the complexes have been established.

THE mid infrared region of copper(II) monohaloacetates have been studied extensively and the work done upto 1978 has been reviewed by Nakamoto[1] and Catterick *et al*[2]. In most of these studies attention was focussed on the shifts of asymmetric and symmetric carboxylate stretching vibrations. Some earlier workers[3-8] assigned a series of bands in the frequency region 400-250 cm^{-1} in copper(II) acetate complexes. However, no attempt has been made to establish or to support the molecular structures of these complexes based on Cu-O vibrations. In our earlier communication[9], we established the dimeric bridged cage structure of some copper(II) *n*-alkanoates, including selection rules to calculate the Cu-O (carboxylate) vibrations in different possible moieties, comparing them with the total number of vibrations actually observed in the spectra of complexes and tentative assignments of Cu-O bands were also proposed, based on normal coordinate analysis. In the present communication an attempt has been made to establish the molecular structures of hydrated copper(II) fluoroacetate, chloroacetate and bromoacetate by studying Cu-O vibrations.

Experimental

The complexes were synthesised by standard methods[10]. The fir spectra were recorded in the region 400-80 cm^{-1} with a Polytech FIR 30 Fourier spectrophotometer. The spectra were recorded at 298 and 77°K. The samples were prepared in wig-shaped polyethylene pellets, obtained by mixing 5.0 mg of a complex with 40 mg powdered polyethylene and pressing.

Results and Discussions

The number of vibrations of the different possible moieties immediately around the Cu atom in the studied complexes have been summarized in Table 1 which shows possible molecular structure, possible moieties around the Cu atom, point-group, type of fundamental vibrations allowed by selection rules and the total number of vibrations which should be active in the spectrum of the complex.

The total number of bands observed in the spectra of the complexes are shown in Table 2. The identification of the bands were made by comparing the spectra of copper(II) haloacetates with those of corresponding sodium salts except those which looked like mixed band, on the basis of increased intensity of the band. All the bands (stretch and bending) due to Cu-O vibrations are believed to lie in the range between 200-500 cm^{-1}. However, to be sure that no relevant band had been overlooked, the supplementary bands below 200 cm^{-1} were also looked for. No supplementary band was observed except in the case of $Cu(ClCH_2COO_2)_2 \cdot 4H_2O$

It is obvious from Table 2 that hydrated copper(II) monohaloacetates show, on the average, 4 bands which agree well with a pyramidal CuO_4 moiety (Fig. 4.2) belonging to C_{4v} point group. We have no exact data about the coordination place of H_2O molecule in these complexes. It is, therefore, considered only tetravalent copper moieties showing the number of bands closest to the observed average 4 and at the maximum 6. Thus the monomeric and dimeric transplanar moieties, CuO_2X_2 (Fig 4.4), and the dimeric square planar structure having CuO_4 and CuX_4 moieties together (Fig. 4.3 and 4.8) need further consideration. To reach clearcut conclusions some other factors should also be taken into account. The monomeric *trans*-planar structure (Fig 4.4) may not be accepted for the

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following reasons :

1. It can not explain spin-spin transition i.e. the subnormal magnetic moment of copper(II) fluoroacetate dihydrate, chloroacetate tetrahydrate and bromoacetate monohydrate are 1.38, 1.45 and 1.48 B.M. respectively[11,12].

2. The existance of band at 375 mμ in uv absorption spectra which is diagnostic of dimeric structure[13].

3. The ΔE (difference between asym. and sym. COO stretching bands) should be much higher, as infact, it has an asymmetrical oxygen and halogen linked bidentate structure, which means a monodentate structure of each COO group. The ΔE values are 195,205 and 202 cm^{-1} for monofluoro, monochloro and monobromoacetates respectively, which are quite close to 184 cm^{-1} for copper(II) acetate monohydrate[14].

TABLE 1—CALCULATIONS OF Cu-O VIBRATIONS IN DIFFERENT POSSIBLE MOIETIES

Molecular structure	Possible moiety	Structure	Figure No.	Point group	Types of vibrations allowed by selection rules	Total no. of active bands
Dimeric bridged cage type ; Cu atom bonded to oxygen	CuO_5	Square pyramidal	4.1	C_{4v}	$3A_1+2B_1+B_2+3E$	6
	CuO_4	Square pyramidal	4.2	C_{4v}	$2A_1+2B_1+B_2+2E$	4
	CuO_4	Square planar	4.3	D_{4h}	$A_{1g}+B_{1g}+B_{2g}+A_{2u}+B_{2u}+2E_u$	3
Monomeric ; Cu atom bonded to oxygen and halogen (X).	CuO_2X_2	*Trans*-planar	4.4	D_{2h}	$2A_g+B_{1g}+2B_{1u}+2B_{2u}+2B_{3u}$	6
	CuO_2X_2	*Cis*-planar	4.5	C_{2v}	$4A_1+3B_2+A_2+B_1$	8
	CuO_2X_2	*Trans*-pyramidal	4.6	C_{2v}'	$4A_1+2B_2+A_2+2B_1$	8
	CuO_2X_2	*Cis*-pyramidal	4.7	C_s	$5A'+4A''$	9
Dimeric bridged cage type : Cu atom bonded to oxygen and halogen (X)	CuO_2X_2	*Trans*-planar	4.4	D_{2h}	$2A_g+B_{1g}+2B_{1u}+2B_{2u}+2B_{3u}$	6
	CuO_2X_2	*Cis*-planar	4.5	C_{2v}	$4A_1+3B_2+A_2+B_1$	8
	CuO_4 CuX_4	Square planar	4.3 4.8	D_{4h}	$A_{1g}+B_{1g}+B_{2g}+A_{2u}+2E_u$	3+3=6
	CuO_2X_2	*Trans*-pyramidal	4.6	C_{2v}	$4A_1+2B_2+A_2+2B_1$	8
	CuO_2X_2	*Cis*-pyramidal	4.7	C_s	$5A'+4A''$	9
	CuO_4 & CuX_4	Square-pyramidal	4.8 4.9	C_{4v}	$2A_1+2B_1+B_2+2E$	4+4=8

O* = HYDROXYL OXYGEN

Fig. 1. Dimeric structure

X = HALOGEN

Fig. 2. Monomeric structure
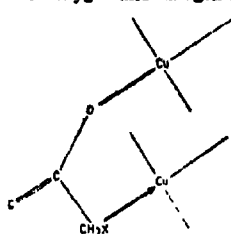
Fig. 3. Dimeric structure

Vibrations in italics are active in infrared.

TABLE 2—TOTAL NUMBER OF Cu-O BANDS OBSERVED IN THE SPECTRA OF COMPLEXES IN THE REGION 500-100 cm^{-1}

Compound	Temp	Number of bands between 500-100 cm^{-1}	Total number of bands observed
$Cu(CH_3CO_2)_2.H_2O$	RT	1vs+3s+1br sh+1w	4–5
	LT	1vs+3s+2m	5–6
$Cu(CH_2FCO_2)_2.2H_2O$	RT	2s+2m+1s mix+1	5–6
	LT	3s+1m+1s mix+1mw	5–6
$Cu(CH_2ClCO_2)_2.4H_2O$	RT	1vs+2s+1m mix+1vw	4–5
	LT	1vs+2s+1s mix+1w	4–5
$Cu(CH_2BrCO_2)_2.H_2O$	RT	1vs+1mw+1vs mix+2s	4–5
	LT	1vs+2s+1vs mix+1m+1vw	5–6

vs = very strong, s = strong, m = medium, mw = medium weak, vw = very weak, w = weak, br = broad, sh = shoulder, mix = mixture, RT = Room temp. (298°K), LT = Liquid nitrogen temp. (77°K).
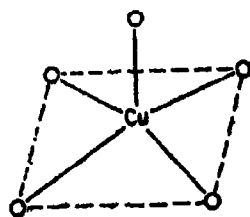
Fig. 4.1 Moiety-CuO_5 square pyramidal point group-C_{4v}.
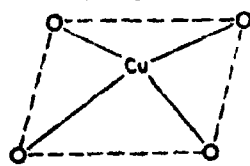
Fig 4.2 Moiety-CuO_4 square pyramidal point group-C_{4v}.
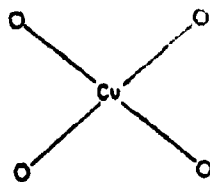
Fig. 4.3 Moiety-CuO_4 square planar point group-D_{4h}.
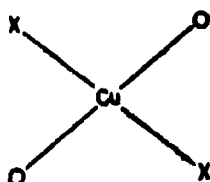
Fig. 4 4 Moiety-CuO_2X_2 *trans*-planar point group-D_{2h}.
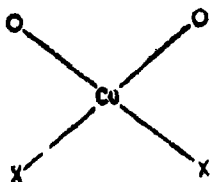
Fig. 4.5 Moiety-CuO_2X_2 *cis*-planar point group-C_{2v}.
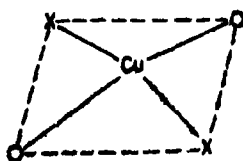
Fig. 4.6 Moiety-CuO_2X_2 *trans*-pyramidal point group-C_{2v}.
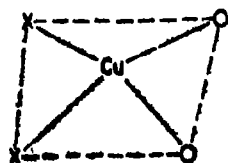
Fig. 4.7 Moiety-CuO_2X_2 *cis*-pyramidal point group-C_s.
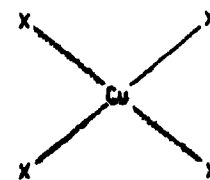
Fig. 4.8 Moiety-CuX_4 square planar point group-D_{4h}.
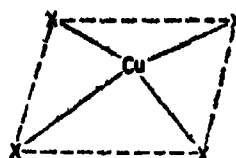
Fig. 4.9 Moiety-CuX_4 square pyramidal point group-C_{4v}.

Fig. 4. Various possible moieties immediately around the copper(II) atom.

The dimeric moieties having *trans*-planar moiety, CuO_2X_2, (Fig. 4.4) belonging to D_{2h} and square planar moieties, CuO_4 and CuX_4 (Fig. 4.2 and 4.8) having D_{4h} point groups, do also not seem reasonable because of the following reasons. :

1. If the molecule has D_{2h} type structure, then all the stretching and bending vibrations will involve halogen (X) atoms except Cu-O stretching vibrations. Thus a bending Cu<(O, X) must be at lower frequency than the bending Cu<(O, O) because F, Cl, Br atoms are heavier than oxygen. In D_{4h} symmetry, 3 vibrations would be due to CuO_4 moiety and 3 to CuX_4 moiety. Thus, 3 vibrations can be in the range of CuO_4 and 3 in the lower range of frequency.
2. The moiety D_{2h} would imply that practically all the stretching vibrations should show their frequencies in the decreasing order Cu-O>Cu-F>Cu-Cl>Cu-Br. A similar trend should be obtained for bendings also. In D_{4h} moiety 3 vibrations should remain fixed and another 3 of planar CuX_4 moiety should show low frequency shifts in the order F>Cl >Br.
3. Both of these moieties have bendings with only one COO oxygen atom, which should also give much higher ΔE values than for bridged cage structures including CuO_4 moieties with bands due to the 2 oxygen atoms of each COO group.
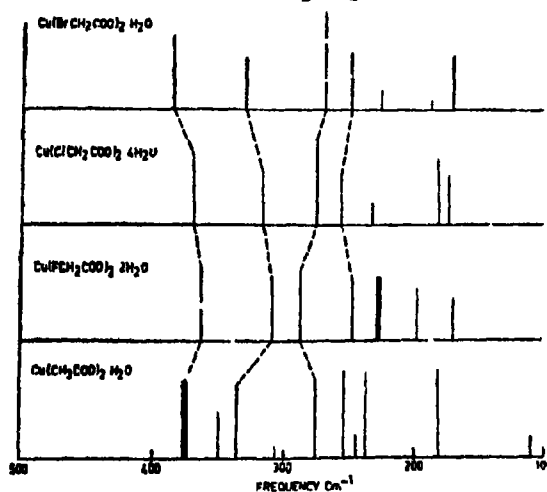
Fig. 5. Comparative chart of copper(II) haloacetates.

A comparative chart of fir region 500-200 cm^{-1} is presented in the Fig. 5. The arguments outlined above can be checked against the trend seen from this figure, taking $(CH_3COO)_2Cu.H_2O$ as the reference.

For D_{2h} moiety, the vibrations should be shifted towards lower frequency in view of points 1 and 2. It is, however, found that monofluoro, monochloro and monobromo compounds have most of the bands shifted to higher frequencies in the sequence fluoro <chloro<bromoacetate. This contradicts the possibility of a dimeric moiety belonging to D_{2h} point group. This conclusion is also supported by ΔE values[14], which are in the range of dimeric bridged cage compounds. All these evidences discard a dimeric structure with local moiety having D_{2h} symmetry around Cu atom.

point for group, as ν_d(Cu-O)>ν_s (Cu-O) > δ_d (O-Cu-O) > δ_s (O-Cu-O).

In Fig. 5, we have presented the comparative chart of copper(II) fluoroacetate, chloroacetate and bromoacetate. The assignments of bands have been made by the proposed theoretical sequence and shown in Table 3. The bands at 364, 370 and 385 cm^{-1} in the spectra of copper(II) fluoroacetate, chloroacetate and bromoacetate are assigned to ν_d(Cu-O) vibrations, whereas bands at 310, 317 and 330 cm^{-1} are assigned to the ν_s(Cu-O) vibration for the respective compounds. Recently, Faniran *et al*[3,5] have assigned the bands at 364 and 324 cm^{-1} for ν(Cu-O) vibrations in copper(II) fluoroacetate. The bands at 385 and 330 cm^{-1} were assigned to stretching modes of Cu-O band in the copper(II) chloroacetate.

TABLE 3—TENTATIVE ASSIGNMENT OF BANDS IN COPPER(II) MONOHALOACETATES

Assignments	$Cu(FCH_2CO_2)_2.2H_2O$	$Cu(ClCH_2CO_2)_2.4H_2O$	$Cu(BrCH_2CO_2)_2.H_2O$
$\nu_d(Cu-O)$	364 s	370 s	385 s
$\nu_s(Cu-O)$	310 m	317 m	330 m
Ring deformation + $\delta_d(O-Cu-O)$	288 s	276 s mix	269 vs
Ring deformation + $\delta_s(O-Cu-O)$	248 m	257 m	248 m mix
Torsion	226 s br mix	233 w	226 w
Lattice vibrations	198 m	182 s	187 small
	170 mw	174 m	170 s

For D_{4h} symmetry, some vibrations should be at nearly fixed positions in monofluoro, monochloro and monobromo compounds and some should decrease in the order acetate>monofluoroacetate> monochloroacetate>monobromoacetate However, we did not find either any fixed vibrations nor any band decreasing from acetate to monobromoacetate. These observations obviate the possibility of local D_{4h} symmetry A similar conclusion is arrived for the point 3 due to low ΔE values which are in the range for the dimeric cage compounds. It is thus concluded that the structure of hydrated copper(II) monohaloacetates should correspond to the CuO_4 moiety with local C_{4v} symmetry (Fig. 4.2)

Tentative assignment of bands : It has been established that in copper(II) acetate monohydrate the moiety immediately around the copper atom is CuO_5 in which the Cu atom is slightly above the plane of the four oxygen atoms making the square pyramidal structure. The four eventual oxygen atoms are at the corners of a square base and the fifth oxygen atom is coordinated to the Cu atom at the transaxial position. The fifth O* atom is of different nature as is shown in Fig. 1. The Cu atom is linked to the other Cu atom by only a very weak δ-interactions. No Cu-Cu bond has, therefore, been considered. The CuO_5 moiety belongs to C_{4v} pointgroup. The fundamental vibrations and their sequence for the CuO_5 moiety of the $Cu(CH_3COO)_2.H_2O$ are: ν_s(Cu-O*) > ν_d(Cu-O) > ν_s(Cu-O) > δ_d(O-Cu-O*) > δ_d(O-Cu-O) > δ_s(O-Cu-O).

On the basis of similar grounds, we named the fundamental vibration and proposed their sequence for copper(II) monohaloacetate, belonging to C_{4v}

It is obvious from Table 3, that both of ν_d(Cu-O) and ν_s(Cu-O) bands shifted to the higher frequency region in the sequence Cu-BAC>Cu-CAC >Cu-FAC; where BAC stands for bromoacetate, CAC for chloroacetate and FAC for fluoroacetate. This sequence leads us to suggest that ν(Cu-O) vibrations decrease with an increase in electronegativity of the R group. This would indicate the weakening of Cu-O bond from bromoacetate to fluoroacetate. A similar behaviour was observed by Nakamoto *et al*[15] for copper(II) acetyl acetonate and copper(II) hexafluoroacetylacetonate. They observed that substitution of CF_3 for CH_3 caused the Cu-O stretching band to shift to a lower frequency. Very recently, Faniran *et al*[3] studying the mono-, di- and trifluoroacetate have pointed out that the Cu-O bond weakens with the increase in the electronegativity of R group On the other hand the frequency separation of ν(Cu-O) vibration [$\Delta\nu$(Cu-O)] is found practically constant for the haloacetates (54, 53 and 55 cm^{-1}) for copper(II) fluoroacetate, chloroacetate and bromoacetate. The same trend was observed for the $\Delta E(\nu_{as}COO - \nu_s COO)$ in these complexes. Therefore, the dimeric bridged cage structure can be established for these complexes.

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Physicochemical Study of Some Transition Metal Complexes of Vanillin-sulphanilate

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Transition metal complexes of a Schiff base, derived from vanillin and sulphanilic acid (Van-Sul), have been prepared and characterised on the basis of element analysis, infrared and electronic spectra and magnetic susceptibility measurements. The magnetic and spectral data indicate them to be low spin octahedral complexes. Van-Sul molecules apparently act as the bidentate O-O donor.

SCHIFF bases containing two or more chromophoric groups separated by only one single bond (i.e. forming a conjugated system) are important not only for their analytical and physiological uses, but also for their interesting spectral and unusual magnetic and structural properties. In continuation of our studies[1-3] on transition metal complexes of Schiff bases derived from vanillin, we report here the results of our studies on the synthesis and characterisation of Fe(II), Co(II), Ni(II), Cu(II), Mn(II) and Fe(III) complexes of Van-Sul.

Experimental

All the chemical used were AR or SM reagents.

Preparation of Van-Sul: On refluxing aqueous solutions of sulphanilic acid and vanillin (hot water) in equimolar ratio, yellow coloured Schiff base, $C_6H_3(OH)(OCH_3)CH{=}NC_6H_4SO_3H$, separated out, m.p. 272° with decomposition, soluble in alkali, alcohol and dioxan.

Preparation of the metal complexes. Metal complexes of the Schiff base were prepared by refluxing aqueous solutions of the metal salt and sodium salt of the Schiff base in 1 : 2 molar ratio for 2 to 3 hr. The metal salts used were $CuSO_4.5H_2O$, $NiSO_4.7H_2O$, $MnSO_4.7H_2O$, $Fe(NH_4)_2(SO_4)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ and $CoSO_4.7H_2O$. Sodium salt of the Schiff base used was prepared by dissolving the Schiff base in the least quantity of a dilute solution of NaOH. The insoluble complexes that separated out on cooling, were filtered, washed, dried in vacuum and analysed for percentage of the metal, C, H, N and S microanalytically.

Results and Discussion

The analytical data and conductometric study indicate 1 : 2 metal : ligand stoichiometry, with the molecular formula $ML_2.2H_2O$, for all the complexes except the iron complex which was shown to have $ML_2(OH).H_2O$ formula. The isolated complexes were insoluble in common organic solvents and water and were infusible below 300°. The magnetic and spectral data indicate these complexes to be low spin ones in which Van-Sul molecules are attached with the metal ion through the phenolic and methoxy oxygen of the vanillin residue and imparting octahedral geometry to the complexes.

Magnetic moments and electronic spectra:

Mn(II)-Van-Sul: The μ_{eff} value (1.7 B.M.) obtained for the complex at room temperature (24°), is well within the range of low-spin octahedral stereochemistry. The electronic spectra of the complex exhibit only two bands at 18.5 kK and 23.2 kK. These low energy bands arising from the ground state $^2T_{2g}(t_{2g}5_{eg}0)$ may be assigned to $^2T_{2g}(I) \rightarrow {}^6A_{1g}(I)$ and $^2T_{2g}(I) \rightarrow {}^2T_{1g}(I)$ transitions respectively, characteristic of octahedral geometry of Mn(II) complexes[4].

Iron complexes: The magnetic moment value obtained for the Van-Sul complex isolated with the Fe(II) salt, is quite abnormal (2.0 B.M.) and is the same as obtained for Fe(III)-Van-Sul (1.97 B.M.). This indicates oxidation of Fe(II) into Fe(III) during isolation, as is also observed in the cases of Van-Hy[2] and Van-An[3] complexes of the salt. The μ_{eff} value of 2.0 B.M. is well within the range reported for spin-paired octahedral complexes of Fe(III)[5,6]. Conclusion that Fe(II) is oxidised to Fe(III) is supported by the electronic and infrared spectra (discussed below) of the complex. The electronic spectra of the complex obtained with the Fe(II) salt show two bands at 17.2 and 20.0 kK which are quite analogous to the band obtained in case of Fe(III) complexes with octahedral stereochemistry[7]. These bands can be assigned to $^2T_{2g} \rightarrow {}^6A_{1g}$ transitions of Fe(III) complexes in octahedral environment. This band in Fe(III) Van-Sul appears at 17.2 kK, in addition to a band at 13.7 kK for the $^2T_{2g} \rightarrow {}^6A_{1g}$ transition. Since the complex isolated with the Fe(II) salt

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did not show any band in the regions 10.5 and 8.0 kK [characteristic of Fe(II) complexes in octahedral stereochemistry], it is clear in the light of the magnetic and spectral studies, that the two complexes of iron isolated in this study have Fe(III) in octahedral stereochemistry.

Co(II)-Van-Sul : The μ_{eff} value (1.78 B.M.) of Co(II)-Van-Sul is characteristic of low-spin octahedral complexes of Co(II). The electronic spectra of the complex indicate two bands, one at 18.9 kK and the other at 20.48 kK and may be assigned to $^2E_g(G) \rightarrow {}^2T_{1g}(G)$ and $^2E_g(G) \rightarrow {}^2T_{1g}$ transitions respectively in octahedral field[8].

Ni(II)-Van-Sul : The magnetic moment of the complex (3.2 B.M.) indicates it to be an octahedral complex[9]. However, the value is higher than that of a typical paramagnetic octahedral Ni(II) complex[9] and indicates large orbital contribution. The octahedral stereochemistry of the complex is also indicated by the two absorption bands seen in its electronic spectra for the transition $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$(16.1 kK) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (28.5 kK).

Cu(II)-Van-Sul : The μ_{eff} value obtained for the complex (1.85 B.M.) is greater than the spin only value (1.7 B.M.) and indicates orbital contribution and distortion of octahedral structure. This complex did not give any band in visible region as d-d transitions are obscured by the intense C.T. bands.

IR spectra : Infrared spectra of the complexes show that the bands due to ν(OH), appearing at 3440, 3180 and 2840cm^{-1} in the free ligand, fuse and become broad in the region 3600-2800 cm^{-1}. The ν(C-O) due to methoxy group, appearing in the region 1240-1290 cm^{-1} in the free ligand, is lowered by 15-30 cm^{-1} in the complexes while ν(C-O) due to phenolic OH group is shifted to higher frequency by 10-20 cm^{-1} in the complexes than in the free ligand. This shows that complexation take place through phenolic OH group with deprotonation[10] and oxygen of the methoxy group. The ν(S-O), and symmetric and asymmetric $\nu(SO_2)$ remain unchanged in the regions 1180, 980 and 1040 cm^{-1}, respectively[11]. The coordinated water in the complexes is indicated by the presence of bands at ~3200, 1600 and 840 cm^{-1} [12,13] while the M-O band appears at ~455 cm^{-1} in the complexes[14].

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Studies on Some Polydentate Ligands. I

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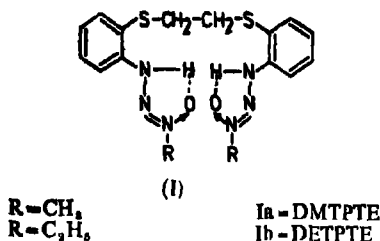
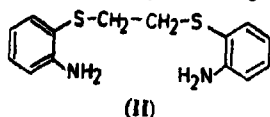
Synthesis and characterisation of two new hexadentate ligands, 1,2-*bis* (*o*-1-methyltriazene-1-oxido-3-phenylthio)-ethane and 1,2-*bis* (*o*-1-ethyltriazene-1-oxido-3-phenylthio)-ethane and their chelates with some bivalent transition metal ions are described.

WE recently synthesised[1] two new hexadentate ligands, 1,2-*bis*(*o*-1-methyltriazene-1-oxido-3-phenoxy)ethane (DMTPE) and 1,2-*bis*(*o*-1-ethyltriazene-1-oxido-3-phenoxy) ethane (DETPE), and their metal chelates with Mn(II), Co(II), Ni(II) and Cu(II). In this communication we report the synthesis and chelating properties of the sulfur analogues of these ligands i.e., 1,2-*bis*(*o*-1-methyltriazene-1-oxido-3-phenylthio)ethane (DMTPTE), (**Ia**) and 1,2-*bis*(*o*-1-ethyltriazene-1-oxido-3-phenylthio) ethane (DETPTE), (**Ib**).

(I)

$R = CH_3$ Ia - DMTPTE
$R = C_2H_5$ Ib - DETPTE

These two ligands act as hexadentate ligands utilising the two sulfur atoms, the two nitrogen atoms linked to the benzene ring and the two oxygen atoms, so that six-coordinate metal chelates of the type M(ligand-2H) are obtained with all the four metal ions, Mn(II), Co(II), Ni(II) and Cu(II).

The synthesis of the present ligands (I) has been achieved by introduction of triazene-1-oxido group in place of the amino group in the ligand (II)

(II)

The synthesis of the above quadridentate ligand (II) was reported by Unger[2] as early as in 1897. Dwyer[3] *et al* in 1967 studied the chelating properties of these ligands.

Experimental

Preparation of ligands : The two ligands were synthesised by coupling the appropriate diazonium salts and substituted hydroxylamine in an acetate buffer at 0°. Details of preparations are as follows.

*1, 2-*bis*(o-1-methyltriazene-1-oxido-3-phenylthio) ethane (DMTPTE) :* 1.75 g of 1,2-*bis*(*o*-aminophenylthio)ethane (II) was taken in 50% hydrochloric acid (4 ml HCl, 4 ml H_2O) and diazotised by 1.15 g of sodium nitrite in 2 ml water. The temperature of the solution was maintained between 0-5°. This diazonium salt solution was added with stirring to 1.12 g of N-methylhydroxylamine hydrochloride in 50 ml of water, cooled to 0°. The *p*H of the reaction mixture was kept in the range 3-5 by slow and simultaneous addition of 7 g of sodium acetate in 20 ml of water. The solution was stirred for 10 more min. After the addition of diazonium salt solution was completed, a pale yellow precipitate separated out. This was filtered and recrystallised from alcohol to yield pale yellow needles. Analysis : C, 48.82 ; H, 5.42 ; N, 21.72 ; S, 16.01. $C_{16}S_2H_{20}N_6O_2$ requires C, 48.97 ; H, 5.14 ; N, 21.42 ; S, 16.34% ; m.p. 169-70°.

1, 2 - bis (o-1-ethyltriazene-1-oxido-3-phenylthio) ethane (DETPTE) : The same procedure was used for the preparation of the DETPTE using N-ethylhydroxylamine hydrochloride as coupling agent. Analysis: C, 51.18 ; H, 5.63 ; N, 19.80 ; S, 15.72. $C_{18}S_2H_{24}N_6O_2$ requires C, 51.14 ; H, 5.75 ; N, 19.99 ; S, 15.25% ; m.p. 171-73°.

Preparation of the complexes :

Manganese(II) complexes : A solution of manganese acetate (1.2 g ; 0.005 *M*) was added to ethanolic solution of ligand (2.0 g of DMTPTE or 2.1 g of DETPTE ; 0.005 *M*). The contents were refluxed for about half an hour and crystalline complexes separated out on concentration. The complexes were washed with hot water and finally with alcohol and dried in a vacuum desiccator over P_4O_{10}. They are insoluble in water and ethanol but soluble in acetone and chloroform.

Cobalt(II) complexes : Aqueous solution of cobalt acetate (1.3 g ; 0.005 *M*) prepared in minimum volume of water was added to ethanolic solution of ligand (2.0 g of DMTPTE or 2.1 g of DETPTE ; 0.005 *M*). The contents were refluxed for about half an hour and red crystalline complexes separated out on concentration. The complexes were washed with hot water and finally with alcohol and dried in

a vacuum desiccator over P_4O_{10}. They are insoluble in water and ethanol but soluble in acetone and chloroform.

Copper(II) complexes : Alcoholic solution of copper(II) acetate (1.0 g ; 0.005 *M*) was added to ethanolic solution of ligand (2.0 g of DMTPTE or 2.1 g of DETPTE ; 0.005 *M*). The contents were refluxed for about half an hour and on concentration, pale red crystalline complexes separated out. The complexes were washed with hot water and finally with alcohol and dried in a vacuum desiccator over P_4O_{10}. These complexes are insoluble in water and ethanol but soluble in acetone and chloroform.

Nickel(II) complexes : Aqueous solution of nickel chloride (1.2 g ; 0.005 *M*) was added to ethanolic solution of ligand (2.0 g DMTPTE or 2.1 g DETPTE ; 0.005 *M*). The contents were refluxed for about half an hour and on concentration, green crystalline complexes separated out. The complexes were washed with hot water and finally with alcohol and dried in a vacuum desiccator over P_4O_{10}. Both the complexes are insoluble in water and ethanol but soluble in acetone and chloroform.

Physical measurements : NMR spectra were recorded on a Varian A-60 spectrometer. Tetramethylsilane was used as the internal standard and frequencies were measured by the side band technique.

Infrared spectra were taken in KBr pellets or in chloroform solutions on a Perkin Elmer 621 spectrophotometer.

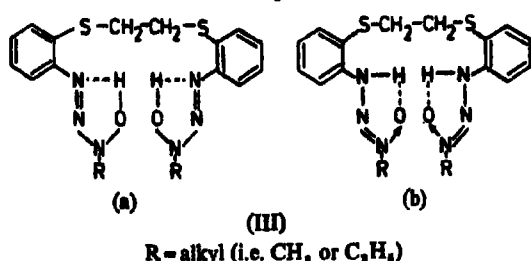
The magnetic susceptibilities were measured on a Gouy balance, using $Hg[Co(NCS)_4]$ as calibrant ($\chi_g = 16.46 \times 10^{-6}$ cgs). The diamagnetic corrections for the ligand atoms and cations were computed using Pascal's constants[10].

Results and Discussion

Structure of the ligands : The two tautomeric forms (IIIa) or (IIIb) are possible for the ligands under discussion. NMR spectra of the two ligands

(a) (b)

(III)

R = alkyl (i.e. CH_3 or C_2H_5)

(DMTPTE and DETPTE) in $CDCl_3$ have a low field signal (-1.4 and -1.5τ), which is of the correct intensity to represent the N-H protons and confirms the existence of the molecule in (IIIb) form. If the ligands exist in (IIIa) form, there must be a singlet for O-H. This is usually located[6,7] at very low field (~ -5τ) while N-H proton is very often found around -3τ. The lowering in the position may be attributed to hydrogen bonding. But no O-H singlet is present in the spectra. So the structure of the ligands can be confirmed as (IIIb) and not as (IIIa).

This examination leads us to conclude that the corresponding compounds having $R = CH_3$ or C_2H_5 are correctly formulated as 1,2-*bis* (*o*-1-alkyltriazene-1-oxido-3-phenylthio)ethane (type IIIb).

Some representative nmr data for the ligands are shown in Table 1. The spectrum of DMTPTE, taken in $CDCl_3$, gives rise to a singlet at 5.95τ representing the two methyl groups. The ethylene group ($-CH_2-CH_2-$) is found to give a singlet at 7.08τ.

TABLE 1—PROTON RESONANCE FREQUENCIES OF THE LIGANDS IN $CDCl_3$

Ligands	Group	Chemical shifts ppm (τ)
DMTPTE	NCH_3	5.95
	$-CH_2-CH_2-$	7.08
	$-C_6H_5$ (aromatic protons)	2.40 – 3.10
	NH	– 1.40
DETPTE	NCH_2CH_3 (due to CH_3 group)	8.45 (t, *J* = 7.5 Hz)
	NCH_2CH_3 (due to CH_2 group)	5.80 (q, *J* = 7.5 Hz)
	$-C_6H_5$ (aromatic protons)	2.30 – 2.55
	NH	– 1.50
	$-CH_2-CH_2-$	7.06

The aromatic protons (in two benzene rings) appear as multiplets in the region 2.40 to 3.10τ. The intensity ratio of the ethylene group and two methyl groups is 1.50.

Similarly, the nmr spectrum of DETPTE in $CDCl_3$ has a low field signal (-1.50τ), which is assignable to the N-H protons. This compound gives rise to one singlet at 7.05τ representing the ethylene group ($-CH_2-CH_2-$). The two methylene groups of C_2H_5 give one quartet in the region 5.50-5.90τ (*J*=7.5 Hz). These signals are assigned to $-N-CH_2-$ on the basis of their chemical shifts at higher field. The two methyl groups of C_2H_5 give one triplet in the region 8.30-8.56τ (*J*=7.5 Hz). The aromatic protons in the two benzene rings give one multiplet in the region 2.30-2.55τ.

Structure of the complexes : All the complexes have 1 : 1 metal : ligand composition. The traizene-1-oxide group is known to act as bidentate. The coordination ability of the thioethereal sulfurs of the ligands is also well established[4-9]. The two ligands may, therefore, act as binegative hexadentate ligands forming neutral six-coordinate complexes (IV).

(IV)

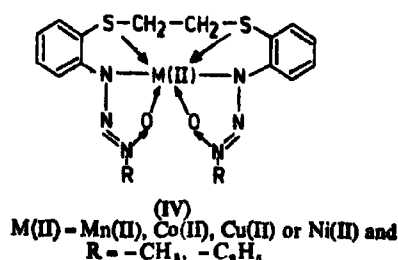
M(II) = Mn(II), Co(II), Cu(II) or Ni(II) and R = $-CH_3$, $-C_2H_5$

The room temperature magnetic moment values (Table 2) for all the complexes are in conformity with such a structure in copper(II), nickel(II) and manganese(II). Complexes show normal magnetic

TABLE 2—ELEMENTAL ANALYSIS AND MAGNETIC PROPERTIES OF THE Mn(II), Co(II), Cu(II) AND Ni(II) CHELATES

	Colour	% C Found (Calcd.)	% H Found (Calcd.)	% N Found (Calcd.)	% S Found (Calcd.)	% M Found (Calcd.)	μ_{eff} (B.M.)
Mn(DMTPTE-2H)	Red	43.40 (43.14)	3.99 (4.07)	18.95 (18.87)	14.61 (14.39)	12.05 (12.35)	6.02
Co(DMTPTE-2H)	Red	42.99 (42.76)	4.06 (4.04)	18.57 (18.70)	14.02 (14.26)	13.40 (13.11)	4.50
Cu(DMTPTE-2H)	Brown	42.10 (42.32)	3.97 (3.99)	18.32 (18.51)	14.43 (14.13)	13.79 (13.99)	1.84
Ni(DMTPTE-2H)	Green	42.53 (42.78)	4.07 (4.04)	18.90 (18.71)	14.45 (14.27)	12.85 (13.07)	3.22
Mn(DETPTE-2H)	Red	45.25 (45.66)	4.62 (4.68)	17.51 (17.75)	13.69 (13.54)	11.28 (11.60)	6.11
Co(DETPTE-2H)	Brown	45.60 (45.28)	4.81 (4.64)	17.41 (17.60)	13.75 (13.43)	12.03 (12.34)	4.39
Cu(DETPTE-2H)	Brown	44.62 (44.84)	4.57 (4.60)	17.29 (17.43)	13.08 (13.30)	13.41 (13.18)	1.99
Ni(DETPTE-2H)	Green	45.02 (45.29)	4.56 (4.65)	17.85 (17.61)	13.59 (13.43)	12.61 (12.30)	3.11

moments corresponding to one, two and five unpaired spins, associated with expected orbital contributions.

In an octahedral crystal field, the magnetic moment[11-20] for high-spin cobalt(II) ($S=3/2$) is expected to be 5.2 B.M. at 300 K. Low spin cobalt(II) complexes possess the electronic configuration $t_{2g}^6\, e_g^1$. The magnetic moment is expected[21-23] to be temperature independent and fairly close to 1.9 B.M. However, cobalt(II) complexes can show magnetic moment at room temperature which is in between for the two spin-states and such intermediate values can arise due to any of the following mechanisms:

(i) partial oxidation of cobalt(II) to cobalt(III),
(ii) antiferromagnetic exchange interactions,
(iii) equilibrium between the thermally accessible ^2E_g and $^4T_{2g}$ states i.e., $^4T_{2g} \rightleftharpoons {}^2E_g$

The lowering in the magnetic moment in the cobalt(II) complexes under study as a result of partial oxidation of cobalt(II) to cobalt(III) is ruled out in view of the constancy in the magnitude of magnetic moment within the range of experimental error (± 0.02) for the complexes obtained from three different preparations. The existence of exchange interactions with very bulky ligands of the type used in the present studies could also be ruled out and, therefore, the intermediate values of magnetic moments observed in the cobalt(II) complexes are possibly due to the equilibrium[24-26] between the thermally accessible $^4T_{2g}$ and ^2E_g states. Magnetic measurements at different temperature would have presented a clear picture of the facts.

Visible spectra of all the complexes contain a strong charge transfer absorption with a shoulder at ~19000 cm^{-1}. This prevents appearance of any d-d bands.

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Equilibrium Study of the Mixed Complexes of Uranyl Ion with 3,5-Dinitrosalicylic as Primary and Some Substituted Carboxylic Acids as Secondary Ligands

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The stabilities of simple and mixed complexes of uranyl ion have been studied with 3,5-dinitrosalicylic acid as primary and malic, chlorosuccinic, dimercapto succinic, maleic, methylmalonic, dimethylmalonic, picolinic, dipicolinic or quinolinic acid as secondary ligands by *p*H metric method. Uranyl forms only 1 : 1 complex with maleic, chlorosuccinic and dimercapto succinic acid while 1 : 1 and 1 : 2 complexes are formed with all the other ligands. The relationship between complex stability and ligand basicity has been used to discuss the formation of mixed-ligand complexes.

THERE has been continuing interest over the years on mixed-ligand complexes of metal ions with biologically important ligands[1-4]. Considering the biological significance of uranyl compounds[5-6], the ternary complexes of UO_2^{2+}-amino acids with some carboxylic acids have been studied[7,8]. As a part of systematic study of UO_2^{2+}-complexes with amino acids, pyridine carboxylic, thiodicarboxylic and simple dicarboxylic acids having 2 and 3 coordination sites, we had earlier reported the formation of series of complexes with these ligands[9-13]. We now report the mixed-ligand complex formation, occuring when uranyl ion is mixed with 3,5-dinitrosalicylic acid and other carboxylic acids. In addition, the present work was undertaken to examine the complexing ability of substituted succinic, malonic and pyridine carboxylic acids with UO_2^{2+}-3,5-dinitrosalicylic binary complexes and to discuss the preferential formation of ternary complexes over binary ones.

Experimental

The ligands such as chlorosuccinic, dimercaptosuccinic, methylmalonic, dimethylmalonic, picolinic, dipicolinic and quinolinic acids were obtained from Fluka (Germany). 3,5-Dinitrosalicylic, malic, maleic acids were B.D.H., AnalaR reagents. The purity of the ligands was checked by their melting points. Uranyl nitrate (B.D.H., AnalaR) was dissolved in perchloric acid to prepare stock solution. All solutions were prepared in glass distilled water. Details for the other chemicals and measurement of pH are given in earlier papers[11-14].

Results and Discussion

The proton-ligand and metal-ligand stability constants of the simple complexes were calculated by Irving and Rossotti's method[16]. The mixed-ligand stabilities and other equilibrium constants (Table 1) were evaluated by the method of Ramamoorthy and Manning[17] as outlined earlier[18]. The formation of simple and mixed species of uranyl complexes was the same and relevant equilibria were discussed earlier[18,19]. To illustrate the equilibrium concentrations in the systems containing 3,5-dinitrosalicylic and dicarboxylic acids, Fig. 1 shows the percentage distribution of the complexes formed in UO_2^{2+}-3,5-dinitrosalicylic-dipicolinic acid system as a function of *p*H.
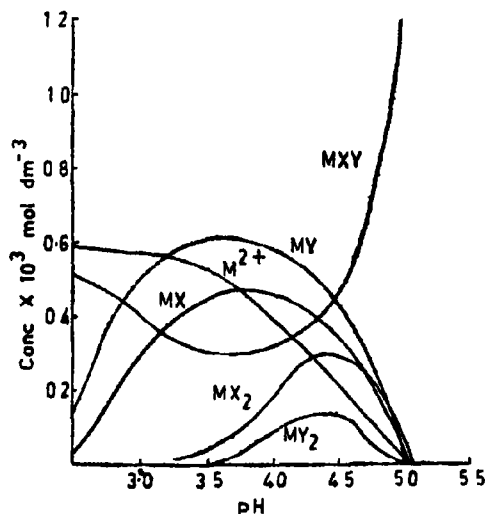
Fig. 1. Distribution of various species present in ternary uranyl ion-3,5-dinitrosalicyclic (H_2Y)-dipicolinic (H_2X) acid system as a function of *p*H. M^{2+} = uranyl ion free, MY = uranyl ion-3,5-dinitrosalicylic, MY_2 = uranyl ion-(3,5-dinitrosalicylic)$_2$, MX = uranyl ion-dipicolinic, MX_2 = uranyl ion-(dipicolinic)$_2$ and MXY = uranyl ion-dipicolinic-3,5-dinitrosalicylic acid. μ = 0.1*M* ($NaClO_4$), Temp. 30±0.1°. $C_M = C_X = C_Y = 2.0 \times 10^{-3} M$.

TABLE 1—LOGARITHMS OF EQUILIBRIUM CONSTANTS OF TERNARY COMPLEXES OF UO_2^{2+}-3,5-DINITROSALICYLIC** (H_2Y)-SECONDARY (H_2X) LIGANDS

Temp. 30° μ = 0.1 M ($NaClO_4$)

Standard deviations are given in parentheses

Secondary ligand/acids	β_{XY}	K_{DXYB}	K_{SYX}	K_{SXY}	$K_{MX_1}^*$	$K_{MX_2}^*$	Δ log K
Malic	10.37(3)	0.24	3.98	4.87	5.50	3.63	−1.52
Chlorosuccinic	8.70(1)	0.39^b 1.26^a	2.31	5.13	3.57	–	−1.25
Dimercaptosuccinic	8.41(3)	0.41^b −1.24^a	1.82	5.15	3.06	–	−1.24
Maleic	10.15(2)	0.26^b −1.39^a	3.76	5.00	5.15	–	−1.39
Methylmalonic	11.53(2)	0.50	5.14	4.83	6.70	4.22	−1.56
Dimethylmalonic	11.27(2)	0.52	4.88	4.95	6.32	4.05	−1.44
Picolinic	9.69(3)	0.04	3.30	5.23	4.46	3.75	−1.16
Quinolinic	9.80(3)	0.16	3.40	5.15	4.65@	3.65@	−1.25
Dipicolinic	11.48(4)	0.58	5.09	6.04	5.44	5.24	−0.35

a = $MX_2 + MY_2 \rightleftharpoons 2MXY$, b = $MX + MY_2 \rightleftharpoons MXY + MY$ and c = $MX + MY \rightleftharpoons MXY + M$

** log K_{MY_1} = 6.39 and log K_{MY_2} = 4.74

* ref. 11.

@ ref. 10.

In the system studied, all the ligands form 1 : 1 and 1 : 2 chelates except maleic, chlorosuccinic and dimercapto succinic acids. 3,5-Dinitrosalicylic acid can be considered as primary ligand and malic, maleic, chlorosuccinic, dimercaptosuccinic, methylmalonic, dimethylmalonic, picolinic, dipicolinic and quinolinic acids, which can respectively form seven, six, seven, seven, six, six, five, five and seven membered rings around the uranyl ion, as secondary ligands Δ log K values (Table 1) are negative for all the systems and indicate the preferential formation of ternary complexes over binary.

During the course of investigation, the order of Δlog K was reported[20,21] as carboxylic-carboxylic. < carboxylic - phenolic < phenolic - phenolic acid systems. In the present work, Δ log K values are intermediate and are in agreement with earlier findings. Sigel[22] reported a method for the estimation of stability constants by the relation between ligand basicity and complex stability. The plots of Δlog K vs Σ pK gave an inverse as well as direct relationship between these two quantities for the mixed-ligand complexes of transition metal ions. These conclusions have been amply confirmed in subsequent studies involving dipeptides and amino acids in aqueous medium[23]. In the systems under investigation, the plot of Δ log K vs Σ pK (Fig. 2) gave direct relationship between these two quantities for closely related ligands. However, the point corresponding to dimethylmalonic acid as secondary ligand deviates from the straight line. The destabilized nature of the mixed-complex in this system is explained on the basis of steric hindrance due to the presence of two methyl groups and two nitro groups in dimethylmalonic acid and 3,5-dinitrosalicylic acid, respectively. In view of this, the higher value of mixed-ligand stability (Table 1) for methylmalonic than that of dimethylmalonic acid system is also understandable.
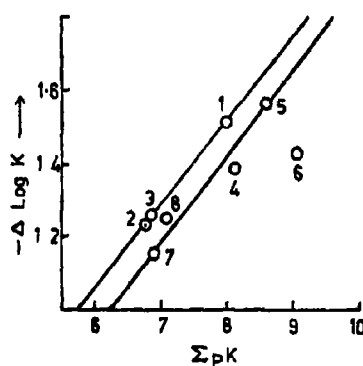
Fig. 2. Relation between Δlog K and ligand stability for ternary complexes of UO_2^{2+}-3,5-dinitrosalicylic carboxylic acids. Carboxylic acids: 1) malic 2) chorosuccinic, 3) dimercaptosuccinic, 4) maleic 5) methylmalonic, 6) dimethylmalonic, 7) picolinic 8) quinolinic. μ = 0.1M ($NaClO_4$), t = 30°.

K_{DXY} values in most of the systems studied here are close to those predicted on statistical considerations. The value of 0.04 of K_{DXY} in 3,5-dinitrosalicylic-picolinic acid system indicates the equal tendency of mixed-ligand formation by disproportionation reaction and dianion to bond 1 : 1 UO_2^{2+} picolinate complex. The values −1.39 and +0.26; −1.26 and +0.39; −1.24 and +0.41 of K_{DXY} for both disproportionation reaction in the system corresponding to maleic, chlorosuccinic and dimercapto succinic acids as secondary ligands indicate the stabilized nature of 1 : 1 UO_2^{2+}-3,5-dinitrosalicylate and ternary complex, respectively.

The formation of ternary complex is mainly dependent on ring size of the chelate which seems to offset the increasing basicity of the secondary ligands observed from the direct relationship between $K_{s YX}$ and the product of the acid dissociation constants for the closely related ligands. The inverse relationship between these two quantities is also reported in our studies on mixed-ligand complexes of uranyl ion involving pyridine carboxylic and dicarboxylic acids as ligands[11,24].

The values of $K_{s YX}$ and K_{MX_s} (Table 1) indicate the formation of mixed complexes over the simple except for the systems involving maleic, chlorosuccinic and dimercaptosuccinic acids as secondary ligands. A comparison of $K_{s XY}$ and K_{MY_s}, especially in the systems involving methylmalonic, dimethylmalonic and dipicolinic acid as secondary ligands reveals the preferential formation of ternary complexes over binary ones.

The order of overall stabilities is methylmalonic dipicolinic > dimethylmalonic > malic > maleic> quinolinic > picolinic > chlorosuccinic> dimercaptosuccinic, which is in accordance with the 1 : 1 binary stabilities. The plots of β_{XY} vs K_{MX_1} (Fig. 3) gave direct relationship. However, the point corresponding to dipicolinic acid complex deviates from the straight line.
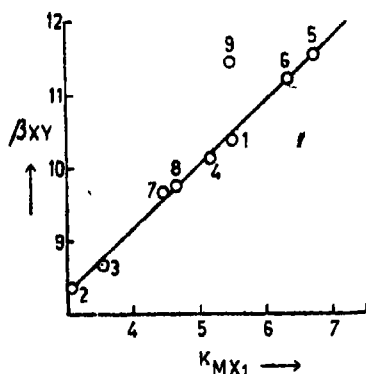
Fig. 3. Relation between β_{XY} and log K_{MX_1} for ternary complexes of uranyl ion with 3,5-dinitrosalicylic and carboxylic acids. Carboxylic acids : 1) malic, 2) chlorosuccinic, 3) dimercaptosuccinic, 4) maleic, 5) methylmalonic, 6) dimethylmalonic, 7) picolinic, 8) quinolinic, 9) dipicolinic. $\mu = 0.1M$ ($NaClO_4$), $t = 30°$.

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Studies on Hydrazones, Semicarbazones, Thiosemicarbazones and Oximes as Ligands. Part-III : Some Divalent Metal Complexes of Benzil Semicarbazone

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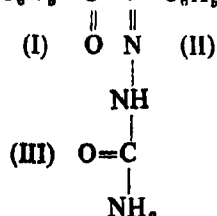
A number of complexes of the composition MLX_2 or ML_2X_2, where M is Mn(II), Co(II), Ni(II), Cu(II), Zn or Cd, X is Cl^-, NCS^- or ClO_4^- and L is benzil semicarbazone have been synthesised and characterised on the basis of analysis, conductance, magnetic susceptibility, infrared and electronic spectral data.

In the programme of preparing complexes of rare and higher coordination number[1(a,b)] ligands with divalent first transition series metal ions, we have been synthesising polydentate chelating ligands since such ligands dominate the area of higher coordination polyhedra in scope and numbers and also from the kinetic and thermodynamic stability point of view. The compact nature of polydentate Schiff bases particularly make them more effective in attaining high coordination structure. Complexation behaviour of bi-, tri- and tetradentate ligands has been reported earlier[1-5]. It was thought worthwhile to have a comparative study of the complexing abilities of hydrazones, semicarbazones, thiosemicarbazones and oximes towards the transition metal ions. As a part of this programme, complexes of benzil phenylhydrazone, 2,4-dinitrophenylhydrazone and oxime have been reported[6-8]. This communication describes some complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn and Cd salts with benzil semicarbazone as the ligand.

Experimental

Benzil semicarbazone $C_6H_5-C(=O)-C(=N-NH-C(=O)-NH_2)-C_6H_5$ with the O of the C=O as (I), the N of C=N as (II) and the O of the semicarbazide C=O as (III)

was prepared by a known method[9]. Analysis of the compound corresponds to benzil monosemicarbazone and its melting point is 242° (against 244°).

Ethanolic solutions of different metal salts were reacted with the ligand in 1 : 2 proportion and the solution refluxed for 30 min to 1 hr. The solutions were concentrated by a rotary vacuum evaporator and kept standing in a refrigerator when crystalline compounds separated out. In some cases addition of petroleum ether was necessary for the isolation of the complexes. These were filtered under suction, washed with absolute ethanol followed by ether and dried in vacuum. Metal, halogen, thiocyanate and nitrogen were estimated as reported earlier[6,7]. Conductance was measured in 10^{-3} acetone solution of the complexes using Toshniwal conductivity bridge. Magnetic susceptibility measurements were made over solid specimens by Gouy method. Infrared spectra were recorded on Perkin Elmer 621 spectrophotometer. Visible electronic spectra were recorded in $10^{-2}M$ chloroform solution of the compounds using Hilger Watt Uvispeck spectrophotometer. The relevant analytical data are presented in Table 1 and some of the spectral data in Table 2.

Results and Discussion

Manganese, nickel and zinc complexes are of the composition MLX_2, whereas copper, cadmium and cobalt complexes are of the formula ML_2X_2. Manganese and zinc complexes are yellowish white, cadmium complexes are white, nickel complexes are deep yellow, copper complexes are light green and cobalt complexes are brown, orange or green in colour. Molar conductance values in acetone medium are low indicating non-electrolytic nature of the complexes, excepting cobalt and cadmium perchlorate complexes which are 1 : 2 electrolytes.

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TABLE 1—ANALYTICAL DATA OF BENZIL SEMICARBAZONE COMPLEXES

Compounds	Λ_M mhos. cm²	% Metal Found	% Metal Calcd.	% halogen, thiocyanate or nitrogen Found	% halogen, thiocyanate or nitrogen Calcd.	μ_{eff} B.M.
1. $MnLCl_2$	10.9	13.58	13.98	17.81	18.07	5.9
2. $MnL(NCS)_2$	8.4	13.32	12.55	26.21	26.49	5.8
3. $MnL(NO_3)_2$	10 2	12.15	12.32	15.54	15.70	5.8
4. $MnL(ClO_4)_2$	10.5	10.36	10.55	7.78	8 06	5.9
5. CoL_2Cl_2	11 2	8.71	8.93	10.38	10.69	4.9
6. $CoL_2(SCN)_2$	9.8	8.14	8.31	16.21	16.36	5 1
7. $CoL_2(NO_3)_2$	7.9	8.05	8.22	15.45	15.62	5 0
8. $[CoL_2](ClO_4)_2$	245	7.25	7.44	10 28	10.60	4 9
9. $NiLCl_2$	10 2	14.51	14.30	17.59	17.90	Diamag.
10. $NiL(SCN)_2$	11.4	13.08	13.29	26.02	26 26	,,
11. $NiL(NO_3)_2$	9 4	12.82	13.06	15.25	15.57	,,
12. CuL_2Cl_2	11.5	9.21	9.50	10.43	10 62	1 78
13. $CuL_2(SCN)_2$	11.2	8 45	8.90	16.11	16 26	1 79
14. $CuL_2(NO_3)_2$	12 8	8.54	8.80	15.34	15.52	1.81
15. $ZnLCl_2$	11.8	16.02	16.21	17.28	17.60	–
16. $ZnL(SCN)_2$	12.5	14.25	14.58	25.48	25 87	–
17. $ZnL(NO_3)_2$	10.8	14 16	14.33	15 21	15 34	–
18. CdL_2Cl_2	9 4	15.42	15.67	9 72	9.90	–
19. $[CdL_2](ClO_4)_2$	242	13.12	13.30	9 75	9.94	–
20. $[ZnL_2](ClO_4)_2$	235	7.85	8.19	10 35	10.52	–

L = Benzil semicarbazone

TABLE 2—SPECTRAL DATA OF SOME COMPLEXES

Compound No.	ν(C=O)	ν(C=N)	ν(N–N)	ν(M–O)	ν(M–N)	ν_{max} in kK (ϵ)
1	1630	1580	1015	460	320	20.4(1), 22.0(2), 24 5(2)
4	1630	1585	1020	465	320	20.2(2), 22 2(2), 24.0(2)
5	1635	1580	1020	470	325	19.8(38), 20.1
8	1630	1590	1020	470	330	19 9(35), 20.4
9	1635	1585	1015	475	330	15 0(58)
12	1630	1580	1020	485	335	14 8(42)
16	1630	1580	1020	480	335	–
19	1635	1585	1015	485	340	–

Magnetic moment values of manganese complexes are in the range of 5.8–5.9 B.M. Cobalt complexes have moments in the range 4.9–5.1 B.M., suggesting an octahedral environment. Nickel complexes are diamagnetic and copper complexes have μ_{eff} values in the range 1.78–1.82 B.M. Infrared spectra of benzil semicarbazone have main absorption bands at 3130, 1655, 1650, 1600 and 1000 cm^{-1} assignable[10] to ν(N–H), ν(C=O), ν(C=N) and ν(N–N), respectively. ν(N–H) in the complexes remains almost unaffected excepting in the chloro complexes where a lowering of the band occurs possibly due to hydrogen bonding with the anion. ν(C=O) is observed around 1630 cm^{-1} along with a shoulder at 1645 cm^{-1} probably indicating[11] the coordination through the oxygen atom of one of the carbonyl group, the other carbonyl remaining free. ν(C=N) in the complexes also shifts to lower frequency region and is observed around 1580 cm^{-1} suggesting coordination through the azomethine nitrogen atom. This has been further substantiated by the observation[12] of ν(M–O) and ν(M–N) around 460-485 and 320-340 cm^{-1} region. Thus, the ligand behaves as bidentate in all the cases excepting the cobalt perchlorate complex where only one carbonyl absorption is observed. Hence, the ligand in this complex coordinates through the oxygen atoms of both the carbonyl groups and the azomethine nitrogen atom indicating the tridentate nature of the ligand.

In the thiocyanato complexes ν(C≡N) is found around 2090-2105 cm^{-1} region, showing[13] the presence of terminal N-bonded thiocyanato group. Nitrato complexes have the ν_1 and ν_4 bands in the 1280 and 1410 cm^{-1} region, respectively. The difference, $\Delta\nu$, is of the order of 130 cm^{-1} suggestive[14,15] of monodentate nitrate coordination. In the cadmium, zinc and cobalt perchlorate complexes there is one broad absorption band at 1100 cm^{-1} indicating[16,17] ionic perchlorate group in conformity with the molar conductance data suggestive of 1 : 2 electrolytic nature of the complexes.

In the visible electronic spectra of manganese complexes three absorption bands are observed around 20.0, 22.0 and 24.0 kK regions assignable[18] to $^6A_1 \rightarrow {^4T_1}(G)$, $\rightarrow {^4T_2}(G)$ and $\rightarrow {^4A_1}(G)$ transitions respectively. Extinction coefficient values are within 1 and 2. Thus, on the basis of the band positions and intensity, tetrahedral structure is presumed for these complexes. All the cobalt complexes give rise to one absorption band around 19-20 kK region with a shoulder on the high frequency side, attributable[19] to $^4T_{1g}(F) \rightarrow {^4T_{1g}}(P)$ transition, the shoulder may be the consequence of splitting due to spin orbit coupling. Lower energy

bands due to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ could not be recorded due to limitations of the instrument. Hence, on the basis of the spectral bands, their intensity and magnetic moment values, a spin free octahedral stereochemistry is suggested for these complexes. Nickel complexes exhibit one absorption band around 14.5-15.0 kK region with extinction coefficient values round about sixty. A square planar configuration is assigned[20] to these complexes in conformity with the diamagnetic nature of the compounds. All the copper complexes exhibit one broad absorption band in the 14.8-15.5 kK regions indicating a distorted octahedral configuration[21]. On the basis of analysis, conductance and infrared spectral data, the zinc and cadmium complexes have presumably a tetrahedral environment around the metal ions. Thus in case of all the complexes possibly the ligand is bonded to the metal ions at site I and II excepting the cobalt perchlorate complex where the metal ion is bonded at site III in addition to site I and II.

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Characterization of Alumina—A Versatile Catalyst

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Different samples of alumina were prepared by impregnating pure alumina with potassium and fluoride ions and their heats of adsorption by adsorption of pyridine were determined by pulse flow technique in gas chromatograph in the temperature range 180-250°. The heats of adsorption decreased with addition of potassium and increased with addition of fluoride ions. Pure alumina had considerable total acidity; however, the Brönsted acidity was negligible.

Rate of dehydration of cyclohexanol was faster initially and decreased with increasing contact time. Cyclohexene, an intermediate registered a maximum at an intermediate contact time and then began to fall, while 1- and 3-methylcyclopentenes kept on increasing; the concentration of 1-methylcyclopentene was always higher than that of 3-methylcyclopentene. The dehydration of cyclohexanol followed a first order kinetics.

The mechanism of transformation of cyclohexanol over alumina has been explained in terms of both Brönsted and Lewis acid sites.

ALUMINA as catalyst or as catalyst support finds multiple uses in several important industrial processes like, dehydration, isomerization, cracking, polymerization, condensation and alkylation[1]. Alumina samples obtained from different sources are found to possess different activities[2]. The presence of acid sites over alumina has been acknowledged, though the nature of acidity, whether Brönsted or Lewis type has been a point of controversy[2-5]. Further, reactivity and selectivity of the catalytic alumina change with the impregnation of alkali or halide ions[1,6].

An attempt has been made in the present work to correlate the activity of different alumina samples obtained by impregnation of pure alumina (from aluminium isopropoxide) with potassium and fluoride ions, with their heats of adsorption of pyridine, as it is a measure of the strength of acid sites. Cyclohexanol was chosen for this purpose because its transformation involves dehydration and skeletal and double bond isomerizations. Some of the steps are explained satisfactorily in terms of Lewis acid sites whose importance in bringing about various isomerization reactions has not been well recognised.

Experimental

Preparation of materials: Alumina A, was prepared by hydrolysing aluminium isopropoxide with distilled water[7]. The precipitated aluminium hydroxide was filtered, washed thoroughly, cut into cakes and dried at 120° for 24 hr. The dried material was then activated at 500° in a stream of pure air for another 24 hr. The activated catalyst was crushed, powdered and sieved to 40-60 mesh size. A part of this material was used as such under the label catalyst A, and the rest was modified with potassium or fluoride ions.

Aluminas B and C were obtained by doping alumina A with potassium nitrate solution in water to give 0.9 and 2.2% by weight of K^+ as K_2O in the catalyst, respectively. Alumina D was prepared by impregnating alumina A with hydrofluoric acid (40% solution, E. Merck) to give 5% by weight of HF in the catalyst. The samples were dried and activated as described earlier.

Apparatus and procedure: The surface area(BET), pore volume and average pore radius of the catalysts were determined by low temperature adsorption of nitrogen[8] and the results are presented in Table 1. The pulse flow technique of Eberly[9,10] was used to measure the heats of adsorption of pyridine on the various aluminas in the temperature range 180-250° and the results are given in Table 2. The total

TABLE 1—SURFACE PROPERTIES OF THE CATALYSTS SUCH AS SURFACE AREA, PORE VOLUME AND AVERAGE PORE RADIUS

Catalyst	S_{BET} m²/g	V_p ml/g	r Å
A	139	0.435	55
B	129	–	–
C	135	0.275	40
D	125	0.442	60

TABLE 2—HEATS OF ADSORPTION OF PYRIDINE (ACIDITY INDEX) AND ACTIVATION ENERGY

Catalyst	Heat of adsorption kcal/mole (acidity index)	Activation energy kcal/mole
A	17.6	1.20
B	9.2	1.06
C	6.2	0.70
D	22.9	0.70

acidity of aluminas A and D was determined by *n*-butylamine titration methods of Johnson[11] and are found to be 0.650 and 1.240 m mole/g, respectively. Brönsted acidity of alumina A was found to be only 0.02 m mole/g by potassium iodide-potassium iodate method[12].

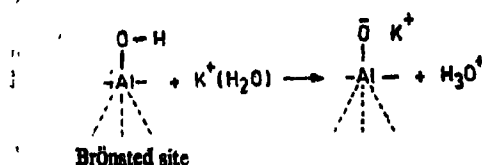
The reactions were carried out in a flow type fixed bed reactor. The operating variables, such as space velocity and particle size, were so chosen as to eliminate diffusion control on the reaction rate. The products were identified by Perkin-Elmer Infracord Model-137 and Perkin-Elmer Vapour Fractometer-154D and estimated using a 2 metre column of Bentone-34 in the Vapour Fractometer-154D.

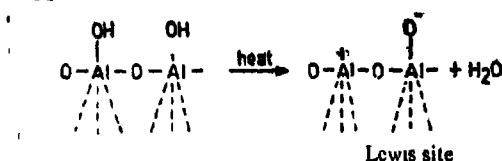
Results and Discussion

The heat of adsorption of pure alumina is found to decrease markedly from 17.6 kcal to 9.2 kcal by the addition of 0.9% by weight of potassium ions. When the doping increases to 2.2% the heat of adsorption falls still further to 6.2 kcal. On the other hand impregnation of alumina A with fluoride ions increases the heat of adsorption from 17.6 kcal to 22.9 kcal.

If the acidic sites on alumina are visualized as protons of the Al-O-H bond (Brönsted acid site), potassium, by replacing the protons in the hydroxyl group, reduces the concentration of Brönsted sites as shown below

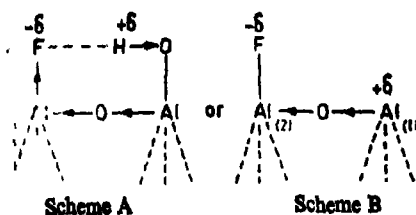
$$\text{O-H} \quad -\text{Al}- + K^+(H_2O) \longrightarrow \bar{O}\ K^+ \quad -\text{Al}- + H_3O^+$$

Brönsted site

Lewis acidity of the dehydrated alumina surface has been explained on the basis of incompletely coordinated aluminium atoms, and its formation is suggested to be as follows :

$$\text{O-Al(OH)-O-Al(OH)-} \xrightarrow{\text{heat}} \text{O-}\overset{+}{\text{Al}}\text{-O-Al(}O^-\text{)-} + H_2O$$

Lewis site

Introduction of potassium ions in the places of hydrogen during the preparation of the catalyst suppresses the formation of Lewis sites. This explains the lower heats of adsorption in the cases of aluminas B and C.

Hydrofluoric acid can enhance the acidic strength of the active sites in one or both of the following ways[13] :

$$\overset{-\delta}{F}\text{----}\overset{+\delta}{H}\rightarrow O \quad \text{Al}\leftarrow O \leftarrow \text{Al} \quad \text{or} \quad \overset{-\delta}{F}\text{-}Al_{(2)} \leftarrow O \leftarrow \overset{+\delta}{Al}_{(1)}$$

Scheme A Scheme B

In scheme A, the acidity of the proton is enhanced by the polarization induced in the adjacent bond by fluorine. In addition, the positive charge on the proton will be stabilized by the partial negative charge on fluorine. In scheme B, the fluorine attached to $Al_{(2)}$ polarises the Al-O-Al bonds in the manner illustrated above and increases the Lewis acid strength of $Al_{(1)}$.

The influence of contact time (W/F) on the rate of dehydration of cyclohexanol and the formation of products has been studied at 375° over alumina A and the results are illustrated in Fig. 1. The rate of dehydration is faster in the lower contact time regions. It decreases slowly and remains constant beyond 0.3 hr. The concentration of cyclohexene increases in the product, registers a maximum around 0.05 hr, and falls with further increase in contact time. Methylcyclopentenes begin to appear after 0.1 hr and keep on increasing ; the concentration of 1-methylcyclopentene is always higher than that of 3-methylcyclopentene.

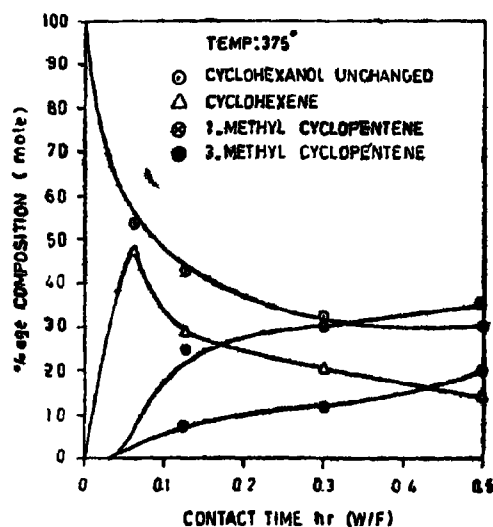



Fig. 1. Influence of contact time on the reactions of cyclohexanol ; Catalyst Alumina A, Temp. 375°.

The effects of acidity index and temperature on the overall conversion of cyclohexanol are shown in Fig. 2. Increase in the acidity index of the catalyst and reaction temperature increases the conversion of cyclohexanol. However, at a fixed acidity index, more cyclohexanol reacted at higher temperature. Even though dehydration occured over low acidity index alumina, it increased considerably with increasing acidity.

The extents of different reactions such as dehydration, skeletal isomerization and double bond isomerization as a function of acidity index are illustrated in Table 3. The most striking features of these results are the different rates at which the activity of aluminas in the various reactions are suppressed when its acidity is progressively reduced. The dehydration activity decreased steadily with increasing additions of potassium ions, while the skeletal and double bond isomerization activities fell

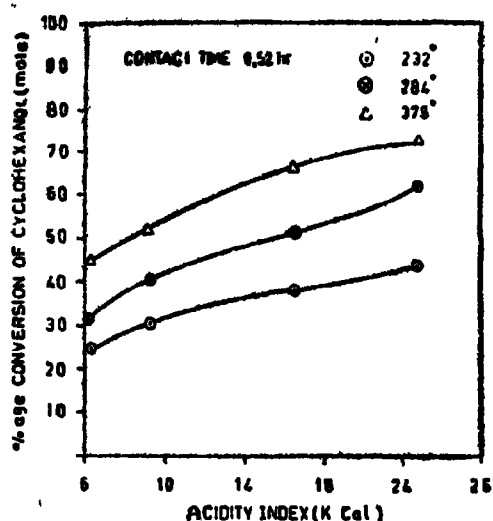



Fig. 2. Influence of acidity index and temp. on the conversion of cyclohexanol.

TABLE 3—COMPARISON OF DIFFERENT REACTIONS SUCH AS DEHYDRATION, SKELETAL ISOMERIZATION AND DOUBLE BOND ISOMERIZATION AS FUNCTION OF ACIDITY INDEX; TEMP. 375°, CONTACT TIME 0.52 hr.

Acidity Index kcal/mole	6.2	9.2	17.6	22.9
Dehydration (mole %)	43.00	51.00	68.00	75.00
Skeletal isomerization (mole %)	0.00	4.00	55.00	55.00
Double bond isomerization (mole %)	0.00	0.00	20.00	20.00

sharply; the fall in the double bond isomerization activity is greater than that of skeletal isomerization activity.

The selectivity ratio (S R) of the catalyst as a function of acidity is given in Fig. 3. The concentration of cyclohexene drastically decreased with increasing acidity index of the catalyst while the concentration of methylcyclopentenes increased and consequently the selectivity ratio decreased.

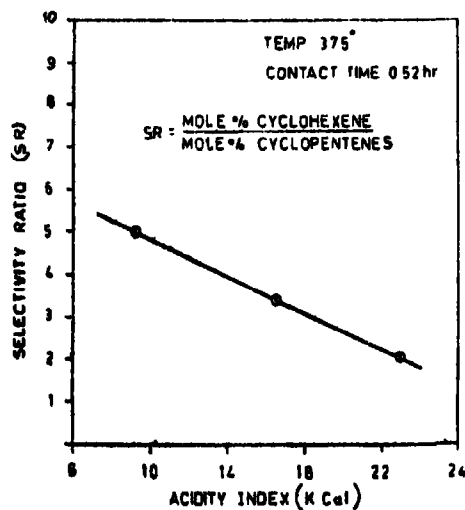



Fig. 3. Influence of acidity index on the selectivity ratio.

The kinetics of dehydration of cyclohexanol over alumina A has been followed by plotting $-\ln(1-X_A)$ (where X_A is the mole fraction of cyclohexanol disappeared) against contact time W/F at 375° (where W is the weight of the catalyst and F is the amount of cyclohexanol fed into the reactor per hour). The plot gives a straight line (Fig. 4) indicating that the reaction follows a first order kinetics. The rate constant calculated from the slope of the first order plot is 2.065 hr^{-1}. The variation of rate constant with temperature is illustrated in Fig. 5 and the energy of activation computed from the slopes of the Arrhenius plots are recorded in Table 2.

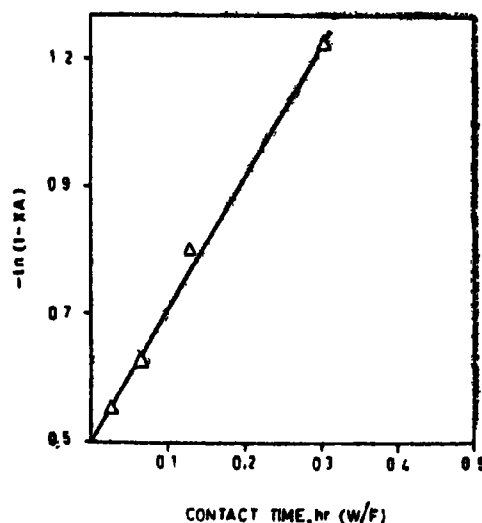



Fig. 4. First order plot; catalyst Alumina A, Temp. 375°.

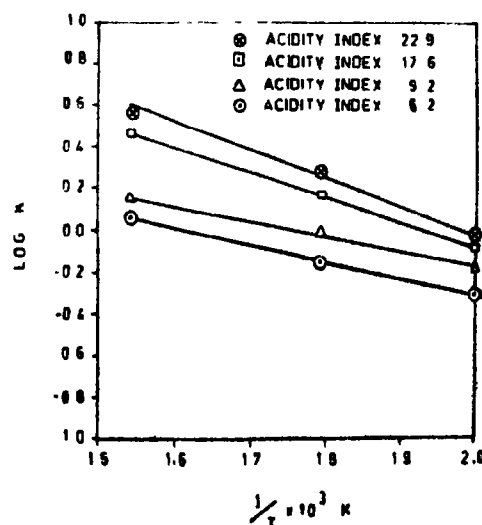
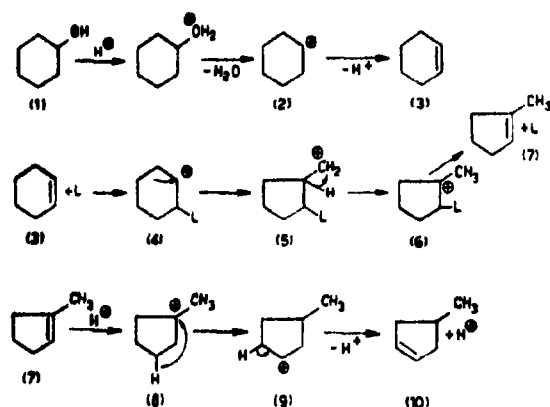



Fig. 5. Arrhenius plots.

Mechanism: Both Dewing[8] and Pearson[4] claim to have detected the presence of Brönsted acid centres on alumina while Knözinger[8] has concluded that alumina possesses no such species. The presence of Lewis acid sites over alumina surfaces and also its importance in bringing about reactions, such as

different types of isomerizations of olefins[14] are well recognized. Further, determination of acidity of alumina shows that it possesses a very significant amount of total acidity. However, the presence of Brönsted acidity is much too small (vide Experimental). In view of the above, the mechanisms of reactions involving the transformation of cyclohexanol are explained both by Brönsted and Lewis acid sites.

The reaction of cyclohexanol is known to proceed by a consecutive reaction, in which cyclohexene, formed initially by dehydration of cyclohexanol, undergoes skeletal isomerization to 1-methylcyclopentene. This may subsequently isomerize to 3-methylcyclopentene by shifting of double bond.

Scheme

The mechanism involves initial protonation of cyclohexanol, the proton coming from the Brönsted acid site of the catalyst, followed by dehydration with the formation of a carbonium ion. Cyclohexene desorbs from the surface with simultaneous elimination of a proton. The cyclohexene adsorbs onto a Lewis acid site resulting in the formation of a carbonium ion which suffers skeletal isomerization involving a less stable primary carbonium ion, which rearranges to a more stable tertiary carbonium ion by 1,2-hydride shift. This then desorbs as 1-methylcyclopentene. The 1-methylcyclopentene is attacked by a proton leading to the formation of a tertiary carbonium ion, which changes to a secondary carbonium ion by 1,3-hydride shift. This eliminates a proton giving rise to 3-methylcyclopentene. The fact that 1,3-hydride shift is not so easy as the 1,2-hydride shift, accounts for the lower concentration of 3-methylcyclopentene.

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Studies on the Suppression of Polarographic Maximum of Mn(II) by Some uni- and poly-valent Cations vis-a-vis Their Influence on the Kinetics of the Electrode Reaction of Mn(II)

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Suppression of the polarographic maximum of Mn(II) in 0.05 *M* KCl, which falls in the category of the negative maximum of the first kind, has been attempted using some uni- and poly-valent metal cations, viz, Li^+, Na^+, K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, La^{3+}, Nb^{3+} and Pr^{3+} as suppressors. The electrode reaction of Mn(II) has been found to be quasi-reversible in the presence of different amounts of these suppressors. The values of kinetic parameters (α and $k_{s,h}$) of quasi-reversible electrode reaction of Mn(II) have been calculated by Gellings' method. A decrease in the values of α and $k_{s,h}$ with increasing concentrations of uni- and poly-valent cations shows that the quasi-reversible electrode reaction of Mn(II) tends towards irreversibility. On the basis of molarity, the order of relative efficacies of metal cations in the suppression of the negative maximum of Mn(II) has been established as $M^{3+} > M^{2+} > M^+$.

LAL and Srivastava[1-3] reported that Mn(II) exhibited a negative maximum of first kind in KCl and attempted its suppression by some aliphatic alcohols and also by various cations. They reported that in the presence of Th^{4+} ions, the maximum of Mn(II) is more exalted than suppressed. This observation contradicts the statement[3] that heavy metal cations suppress the maxima more readily than do those of light elements. The central idea of these studies has been to find the optimum concentration at which the maximum is just suppressed and then to formulate an order of efficacies on the molarity scale. Recently, Ram *et al*[4] have attempted the suppression of the maximum of Mn(II) by various ionic (both cationic and anionic) and non-ionic surfactants and compared their relative efficacies in the suppression of this maximum on the basis of their characteristic properties. In the present paper an attempt has been made to suppress the maximum of Mn(II) by some uni- and poly-valent cations and then to study the influence of these cations on the kinetics of the electrode reaction of Mn(II). The order of relative efficacies of uni- and poly-valent cations in the suppression of the maximum of Mn(II) has been established on the basis of molarity scale of concentration.

Experimental

All the chemicals used were of reagent grade and their stock solutions were prepared in conductivity water. The concentration of Mn(II) (using $MnCl_2 \cdot 2H_2O$) was kept at 1.0×10^{-3} *M* in each case. 0.05 *M* KCl was used as the supporting electrolyte. The polarograms of the solutions were taken on a manual set-up[5]. Stock solutions (2 *M*) of Li, Na, K (as nitrates) and of Ba, Sr, Ca and Mg (0·1 *M*) (as nitrates) were prepared by direct weighing from A.R., B.D.H., samples. The concentrations of the rare earth cations (as nitrates) in their stock solutions were determined by standard methods[6-7]. Solutions of desired molarity were prepared from these stock solutions of known concentrations by dilution.

The experimental conditions such as the concentration of the depolarizer, the concentration of the supporting electrolyte (KCl), *p*H and the height of mercury column were adjusted in such a way as to obtain a sharp and well-defined maximum of Mn(II). These conditions were kept the same in all the cases throughout the study. Thus, the concentration of the depolarizer was kept at 1.0×10^{-3} *M*, that of the supporting electrolyte at 0.05 *M*, the *p*H of the medium at 6.0 (by adding very dilute solutions of HCl or NaOH) and the height of the mercury column (h_{corr}) at 71.45 cm.

Results and Discussion

The first kind polarographic maximum of Mn(II) under the chosen experimental conditions appears at -1.53V (vs S.C.E.). This lies well on the negative side of the electro-capillary curve and hence the maximum of Mn(II) is of negative polarity[8]. Representative Fig. 1 depicts the morphology of

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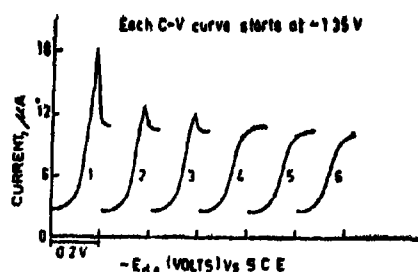
Fig. 1. C-V curves of Mn(II) in the presence of increasing concentrations of Mg^{2+}.
1. 0.0 *M*, 2. 0.7×10⁻³ *M*, 3. 1.1×10⁻³ *M*, 4. 1 2×10⁻³ *M*, 5. 2.8×10⁻³ *M*, 6. 4.0×10⁻³ *M*.

C-V curves of Mn(II) in the presence of increasing concentrations of Mg^{2+}.

E_{max} of Mn(II) gets shifted to positive potentials (Table 1) with increasing concentrations of uni- and poly-valent cations. The value of i_{max} decreases sharply before the suppression of the maximum, which indicates that the negative maximum of Mn(II) is susceptible to suppression by the requisite amounts of uni- and poly-valent cations. After the suppression of the maximum, Mn(II) yields, in each case, a well-defined wave which is diffusion-controlled.

TABLE 1—POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS FOR THE ELECTRODE REACTION OF Mn(II) IN THE PRESENCE OF INCREASING CONCENTRATIONS OF UNI- AND POLY-VALENT CATIONS AT 25±0.1°.
h_{corr} = 71.45 cm ; t = 3.1 sec ; m = 2 2 mg/sec ; $m^{2/3} t^{1/6}$ = 2.03 $mg^{2/3} sec^{-1/2}$ (IN 0.05 *M* KCl, OPEN CIRCUIT).

[Cation] *M*	$-E_{max}$ (S. C. E.)	$-E_{1/2}$ (S. C. E.)	i_{max} μA	i_d μA	Slope mV	D×10⁶ cm²/sec	α	$k_{s,h}$ (×10³) cm/sec
0.0	1.53	–	15.71	–	–	–	–	–
×10¹				Li^+				
0 8	1 52	–	14.73	–	–	–	–	–
1.6	1 51	–	8 90	–	–	–	–	–
2 0*	No max	1.489	–	7.51	41	6.85	0.80	8.62
11 6	,,	1.493	–	5.70	47	3.95	0.75	5.13
				Na^+				
0.6	1.52	–	14.32	–	–	–	–	–
0.7	1.51	–	7.78	–	–	–	–	–
0.8*	No max	1.489	–	7.64	40	7.11	0.80	7.22
3.2	,,	1 492	–	5.84	44	4.15	0.72	1.55
				K^+				
0 5	1 52	–	12.51	–	–	–	–	–
1.1	1 51	–	7.92	–	–	–	–	–
1.3*	No max	1.495	–	7 41	41	6.85	0.81	6.10
4.8	,,	1.500	–	6 25	45	4 76	0.75	3.14
×10²				Ba^{2+}				
0 2	1 52	–	10.15	–	–	–	–	–
0.3	1.51	–	8.76	–	–	–	–	–
0.4*	No max	1 497	–	7 64	40	7.11	0.84	2.80
5.4	,,	1.500	–	6.39	43	4.97	0.74	2.06
				Sr^{2+}				
0.1	1.52	–	11.26	–	–	–	–	–
0.4	1 51	–	7 92	–	–	–	–	–
0.5*	No max	1.490	–	7 51	40	6 85	0.85	4.08
5.5	,,	1.500	–	6.81	44	5.64	0.68	2.63
				Ca^{2+}				
0.1	1.52	–	10 29	–	–	–	–	–
0.5	1.51	–	8.34	–	–	–	–	–
0.8*	No max	1.480	–	7.23	39	6.36	0.85	8.24
2.3	,,	1.483	–	6.12	42	4.55	0.80	4.41
				Mg^{2+}				
0.7	1.52	–	10.01	–	–	–	–	–
1.1	1 51	–	9.17	–	–	–	–	–
1.2*	No max	1.490	–	7.78	40	7.37	0.83	6.30
4.0	,,	1 493	–	7.23	43	6.36	0.75	5.49
×10⁴				La^{3+}				
0.2	1.53	–	13.48	–	–	–	–	–
0.7	1.52	–	12.10	–	–	–	–	–
1.0	1.52	–	8.48	–	–	–	–	–
1.2*	No max	1.490	–	7.37	40	6.60	0.86	5.20
1.5	,,	1.495	–	6.95	42	5.88	0.75	3.89
				Nb^{3+}				
0.2	1.52	–	13.62	–	–	–	–	–
0.7	1.51	–	9.87	–	–	–	–	–
1.0*	No max	1.490	–	7.51	40	6.85	0.87	5.29
1.5	,,	1.495	–	6.67	42	5.41	0.77	4.89
				Pr^{3+}				
0.6	1.52	–	10.29	–	–	–	–	–
0.9	1.51	–	7.92	–	–	–	–	–
1.0*	No max	1.493	–	6.95	41	5.88	0.88	8.56
2.0	,,	1.495	–	6.81	43	5.64	0.78	6.49

* Concentration at which the maximum just disappears.

A perusal of slope values (Table 1) of log plots shows that the slope values of 2-electron reduction process of Mn(II) lie in the range 39-49 mV which indicates[9-13] that the polarographic reduction of Mn(II) is quasi-reversible in the presence of increasing amounts of uni- and poly-valent cations. The values of kinetic parameters (α and $k_{s,h}$) of the quasi-reversible electrode reaction of Mn(II) have been calculated by Gellings' method[14]. The values of $k_{s,h}$ are of the magnitude of 10^{-3} cm/sec which confirm[15,16] the quasi-reversible nature of the electrode reaction of Mn(II). It is observed that the value of $k_{s,h}$ decreases with increasing concentrations of uni- and poly-valent cations. This shows that the quasi-reversible electrode reaction of Mn(II) tends towards irreversibility with increasing concentrations of uni- and poly-valent cations. It is also evident from Table 1 that the value of α decreases with increasing concentrations of the cations thereby showing that the quasi-reversible electrode reaction of Mn(II) tends towards irreversibility. The variations in the values of $k_{s,h}$ and α thus lead to the same conclusion. Further, a negative shift in $E_{1/2}$ and a decrease in i_d with increasing concentrations of uni- and poly-valent cations lend support to the conclusion arrived at on the basis of the variations in the values of $k_{s,h}$ and α.

By comparing the concentrations (on the molarity scale) of the various uni- and poly-valent cations at the stage where the maximum gets just suppressed, the order for the relative efficacies of various uni- and poly-valent metal cations in the suppression of negative maximum of Mn(II) has been established as $M^{3+} > M^{2+} > M^{+}$.

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Chemisorption Kinetic Studies of Oxygen on V_2O_5-Ti_2O_3

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From studies on the chemisorption of oxygen over V_2O_5-Ti_2O_3 mixture and V_2O_5 separately, it was observed that the mixture exhibited higher activity. With the help of X-ray, DTA and magnetic measurement of the sample an attempt has been made to correlate the enhanced activity with the changed oxidation states. Elovich equation was found to be obeyed in all cases. Attempt has also been made to represent the probable mechanisms of the reaction.

VANADIUM pentoxide is known as an important catalyst for oxidation reactions. Different investigations on the various aspects of V_2O_5 like X-ray structure analysis, adsorption studies, thermal behaviour, catalytic activity etc. has established that the anomalous behaviour of V_2O_5 is due probably to the peculiar geometry [1,2,3] as well as different composition of the oxide. The presence of lower valent states, either singly or in combination with V_2O_5, is responsible for catalytic reaction (oxidation)[4]. However, the existence of lower valent states and the presence of different phases with varying composition make it difficult to attribute the catalytic activity uniquely to any particular oxidation state.

Titanium sesquioxide, Ti_2O_3, isomorphous with V_2O_3 and Cr_2O_3 shows anomalous electrical and magnetic properties related in origin to V_2O_3. It has been observed from a study of the states of TiO_2 heated in vacuum[5] that at 300° it is partially reduced to Ti^{3+} while on heating to 500° and above not only oxygen but also titanium enter gas phase and a compound, $Ti_{1-x}O_{2-y}$, where $y>x$ is formed. This process can lead, on subsequent treatment of the TiO_2 with oxygen, to the development of p-type semiconductivity, though V_2O_5 normally exhibits n-type semi-conductivity. It is assumed that the change in the properties of TiO_2, when treated under various conditions, is caused by a shift of the reaction $Ti^{3+}+O_2=Ti^{4+}/O_2$. Thus, Ti^{3+} defects
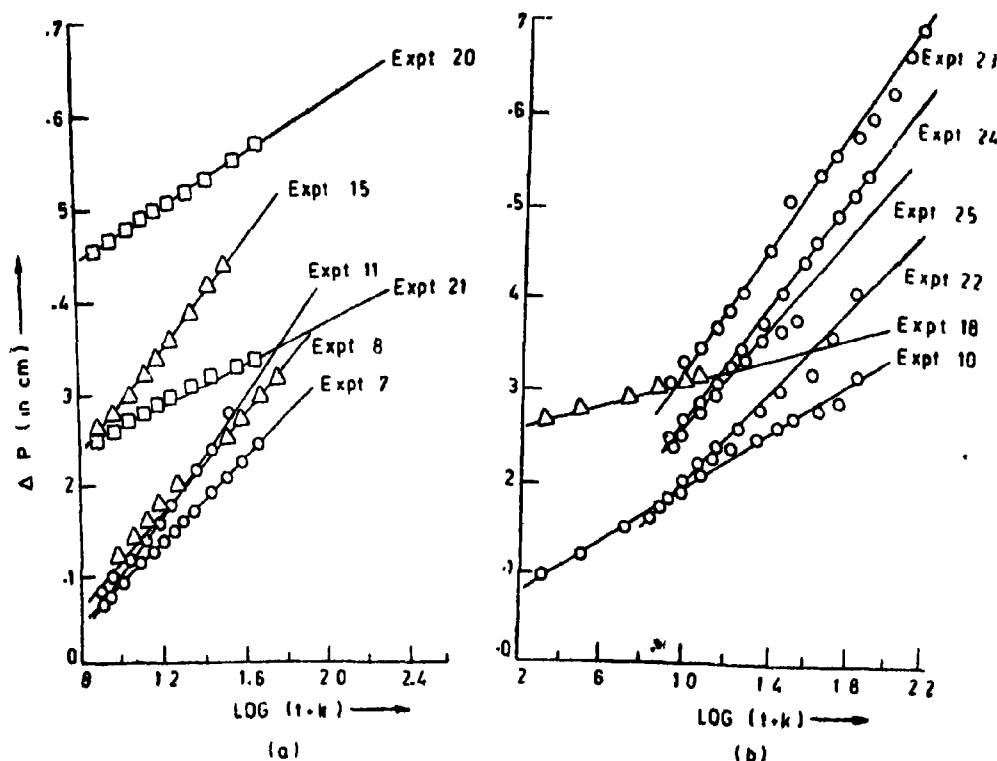
Fig. 1. Plot of Δp vs log (t+k).

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Fig. 2. Absorption isotherms (a) and isobars (b)
Adsorption isotherms (a)
325°—▲...▲—
300°—⊙...⊙—
375°—●...●—
350°—⊡...⊡—
275°—⊗ ⊗—

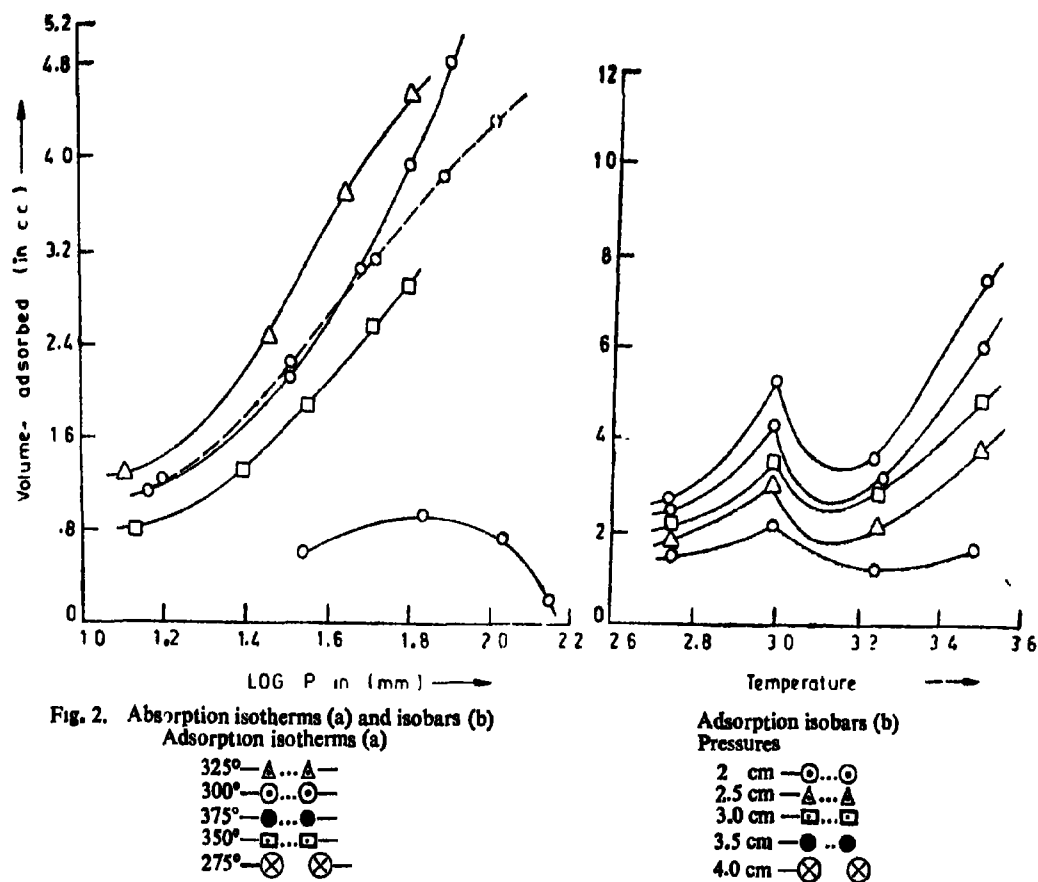
Adsorption isobars (b)
Pressures
2 cm —⊙...⊙
2.5 cm —▲...▲
3.0 cm —⊡...⊡
3.5 cm —● ..●
4.0 cm —⊗ ⊗

appearing on TiO_2 lattice must always be accompanied by the evolution of molecular oxygen which has been found to be true only at temperature of 500° and above.

TABLE 1—MODEL RESULTS OF ADSORPTION OF OXYGEN

Expt. No 7, P_0 = 17.05 cm of Hg, T = 300°		Expt No. 10, P_0 = 27.2 cm of Hg, T = 300°		Expt. No. 8, P_0 = 8.8 cm of Hg, T = 350°	
Time (min)	Δp (cm of Hg)	Time (min)	Δp (cm of Hg)	Time (min)	Δp (cm of Hg)
1	0.07	1	0.10	1	0 08
2	0.08	2	0.12	2	0.10
3	0.10	4	0.15	3	0 12
5	0.12	6	0.17	5	0 14
7	0.13	8	0.19	7	1.16
9	0.14	10	0.21	9	0 18
11	4.15	12	0.23	11	0 20
13	0.16	15	0.24	15	0.22
15	0 17	20	0 25	20	0.24
20	0.20	25	0.26	25	0.25
25	0.20	30	0.27	30	0 27
30	0.21	40	0.28	40	0.30
40	0.25	50	0.29	50	0.32
		60	0.32		

For the present investigation we have used the catalyst V_2O_5 containing Ti_2O_3 in 3 : 1 mole ratio prepared at high temperature. It is certain that Ti^{3+} in the mixture is converted to Ti^{4+} during its preparation. But heating the catalyst in vacuum would again lead to partial reduction and Ti^{3+} formation as in TiO_2. So, V_2O_5 containing Ti_2O_3 as prepared would act as if it is a mixture of V_2O_5-TiO_2. We, thus, aimed to study the effect of incorporation on chemisorption and electrical conductivity studies of V_2O_5 with Ti_2O_3.

Preparation of sample : The sample of V_2O_5 was prepared as described earlier[6] The sample of titanium sesquioxide used was prepared[7] by the reduction of TiO_2 by passing pure, dry hydrogen with titanium tetrachloride at 750° for 48 hr.

The sample of vanadium pentoxide containing titanium sesquioxide, V_2O_5-Ti_2O_3, was prepared by mixing V_2O_5 and Ti_2O_3 in 3 : 1 mole ratio respectively in a porcelain basin at 800°-1000° in nitrogen atmosphere. The resulting product, after cooling, was extracted with oxalic acid, evaporated and decomposed in vacuum. The particle size chosen was −120+140 B.S.S.

Characterisation of the sample : The sample of V_2O_5 was analysed chemically by the method of Caderbank[8] and the sample of Ti_2O_3 was analysed by both volumetric[9] and gravimetric methods. 1.1% of V^{4+} ions were present in the sample of V_2O_5. In the volumetric analysis of Ti_2O_3 calculation on the basis of the equation $V^{5+}+Ti^{3+} \rightarrow V^{4+}+Ti^{4+}$ gave the % of Ti^{3+} in the prepared Ti_2O_3 as 66%. A direct method for gravimetric analysis of the

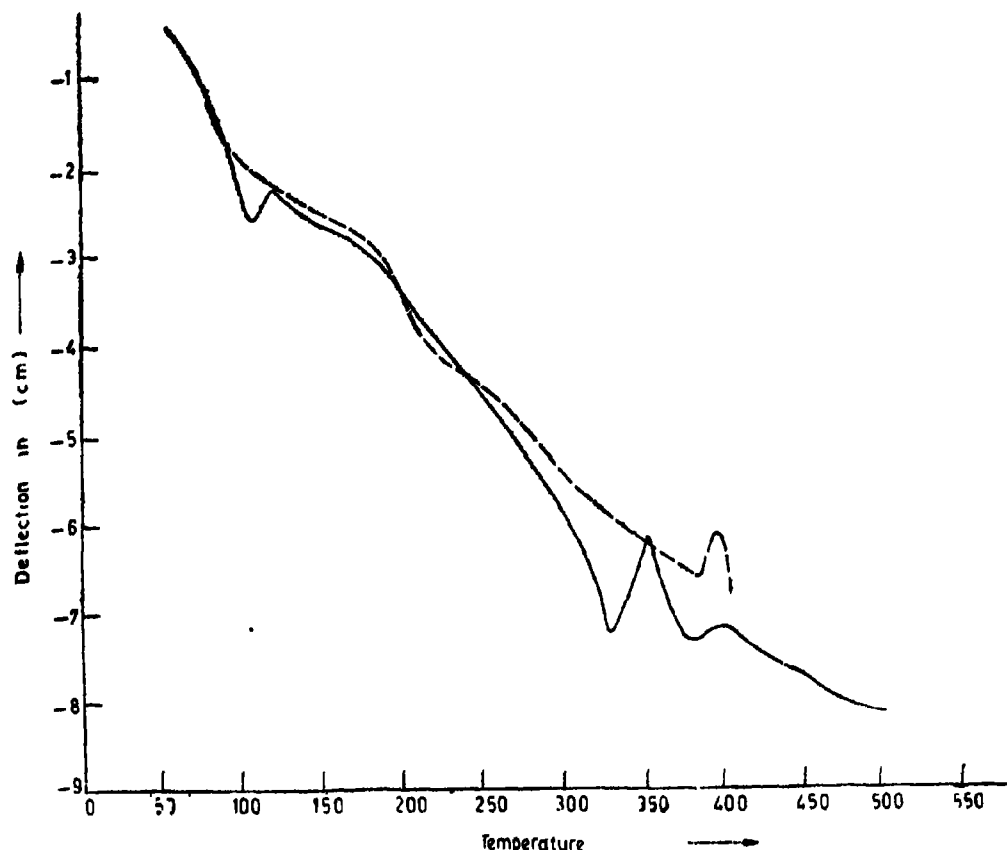



Fig 3 DTA thermograms. Heating curve—— Cooling curve- - - - -

TABLE 2—MODIFIED ELOVICH PARAMETERS

Expt. No	Temp.	Pressures (cm of Hg)	α (cm^{-1} min^{-1})	k (min)	to (min)	a*(a) (cm g min^{-1})	$\Delta p_0'$ (cm)
7	300	17.05	9.979	7	3.860	0.01451	0.0597
15	325	17.05	7.757	7	1.063	0.01842	0.2431
11	350	17.05	7.119	7	58.880	0.02007	−0.2991
24	375	17.05	7.037	7	1.484	0.02031	0.1051
10	300	27.20	15.35	1	0.4861	0.06515	0.047
18	325	27.20	16.89	7	0.003303	0.008460	0.4534
20	350	27.20	15.35	1	0.05413	0.06515	0.195
25	375	27 20	8.011	7	−1.1719	0.01783	0.2167
8	350	8.80	8.80	7	3 394	0.01621	0.0818
22	375	8.80	9.234	7	1.452	0.01547	0 1663
21	350	13.00	21.18	7	0.03442	0.006743	0.2506
23	375	13.00	6.50	7	−1.4084	0 021984	0.2721

TABLE 3—VALUES OF α_1, α_2, α_3, CALCULATED FROM Δp VS LOG t PLOTS

Expt. No.	Temp (°C)	Pressure (cm of Hg)	α(cm^{-1} gm) α_1	α_2	α_3
7	300	17 05	40.64	12 62	–
15	325	17.05	26.90	10 40	–
11	350	17.05	33.91	10 80	–
24	375	17.05	40.68	9 003	–
10	300	27.20	21.08	–	–
18	325	27.20	49.73	–	–
20	350	27.20	30.11	7.754	–
25	375	27.20	30.11	15.25	–
8	350	8.80	24.73	11.74	–
22	375	8.80	21.08	5.27	–
21	350	13.00	31.62	–	–
23	375	13.00	24.84	9.003	6.39

sample, $Ti_2O_3 + \frac{1}{2}O_2 \rightarrow TiO_2$ was done and the value obtained was 99% of the theoretical value.

It is known that V^{5+} is a strong oxidising agent and Ti^{3+} a very strong reducing agent. In the oxide obtained by heating a mixture of V_2O_5 and Ti_2O_3 it is almost certain that Ti^{3+} has been completely oxidized to Ti^{4+} and simultaneously V^{5+} has been reduced to some other lower valent states. Thus no chemical analysis of the sample regarding the oxidation states of the vanadium in it was attempted.

X-ray powder photograph of the specimen was obtained using a 2865 mm dia camera (Philips model PW 1008) and chromium radiation (λ=2.291 Å) in

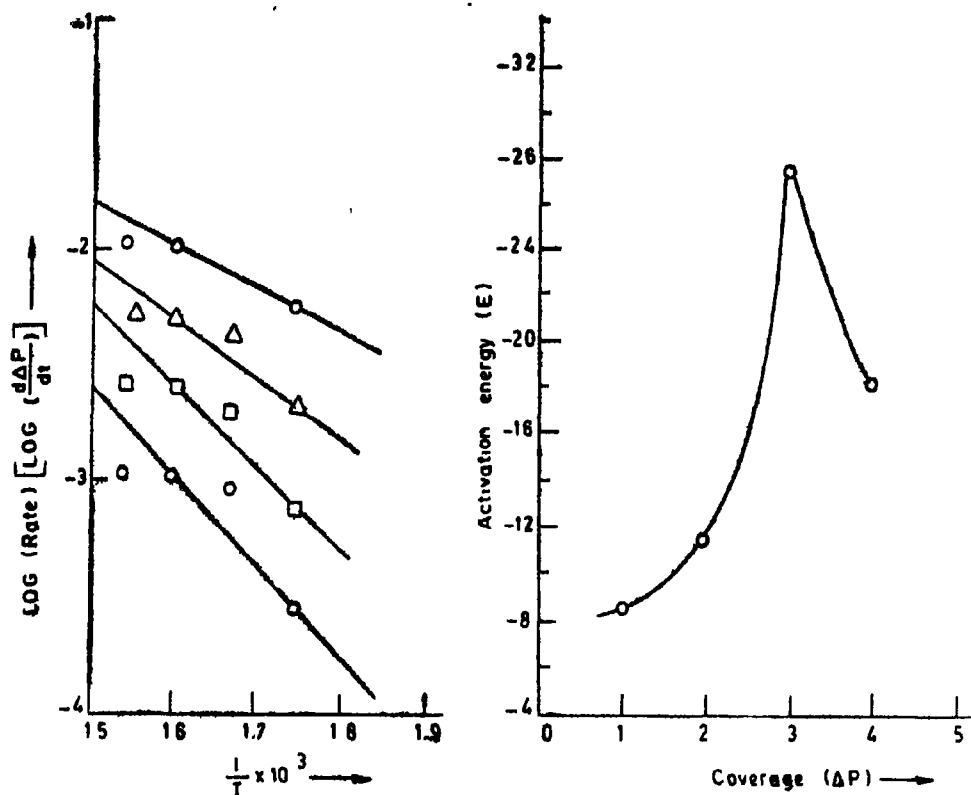
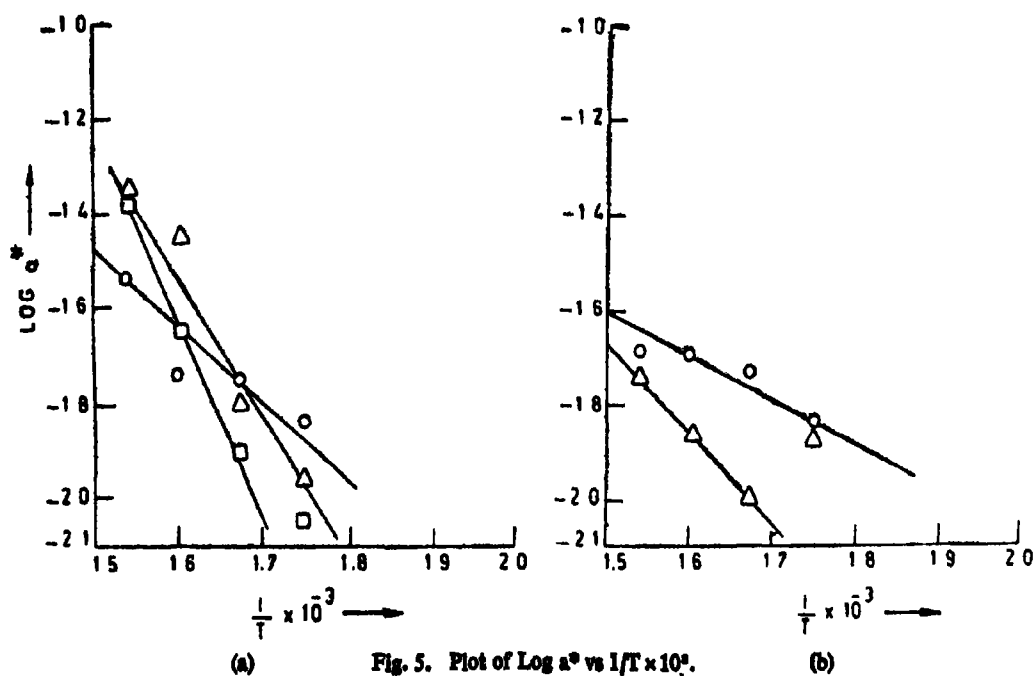



Fig. 4. (a) Plot of log (rate) $\left[\text{Log}\left(\frac{d\Delta p}{dt}\right)\right]$ vs $1/T \times 10^3$. (b) Plot of activation energy (E) vs coverage (Δp).

Δp (.1) —⊙...⊙
Δp (.2) —Δ...Δ
Δp (.3) —□..□
Δp (.4) —⊙...⊙

(a) Fig. 5. Plot of Log a* vs $1/T \times 10^3$. (b)

Expt. 55-60—Δ...Δ
Expt. 46-51—⊙...⊙
Expt. 70-74—□.. □

the absence of any filter. Approximately 6 hr exposure was given at 25 KV and 10 MA. Results are given in Table 4.

TABLE 4—X-RAY ANALYSIS DATA

Sample (After preparation)		Sample (after O_2 kinetics)	
Intensity	d(Å)	Intensity	d(Å)
F (B)		VF (B)	1 383
M	1.685	F (D)	1 738
VF	2.242	VF	1 840
VF	2 479	F	2.269
F	3.152	VF	2.583
		F	3.00
		M	3 388
		M	3.534
		F	4.557
		VF	5.920

Magnetic susceptibility was determined by using a Guoy balance at a field strength of 3.64×10^{8} gauss. Standard DTA analysis was done using

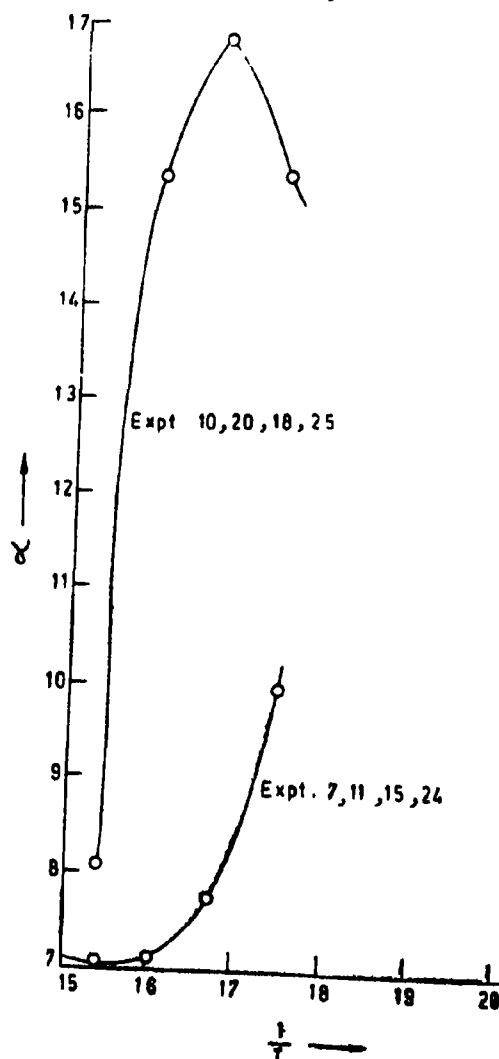



Fig. 6. Plot of α vs 1/T.
17 cm (pressure) —⊙...⊙
27. 2 cm (pressure) —⊕...⊕

γ-alumina as the reference. Surface area measurement was done by conventional BET method using liquid nitrogen and the surface area before and after adsorption were found to be 14.1 m^2/g and 20.2 m^2/g respectively. Oxygen gas used was prepared following the procedure described earlier[8].

Experimental

The method for sample preparation and degassing and the form of the Elovich equation[10,11] applied has been described by De and Gadgil[8]. The kinetic measurements were carried out in the temperature range 275°-375° using oxygen.

Adsorption isotherms were obtained and isosteric heats of adsorption were calculated from the isotherms by the use of Clausius-Clapeyron equations :

$$\text{Log}\,(P_1/P_2)_\theta=\frac{\Delta H_\theta}{4.57}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \quad \ldots (1)$$

where the terms have their usual significance. Isobars have also been plotted.

At temperatures 300° and 325° kinetics proceeds too slowly within the pressure range 4.7-13 cm of Hg. So kinetics was studied at pressures 17.02 and 27.2 cm of Hg. All other measurements were done between 4.7-27.2 cm of Hg.

Results and Discussion

Chemisorption of oxygen does not proceed at low temperatures and pressures over this sample. Adsorption starts at 300° for an initial pressure of 17 cm and 27.2 cm of Hg, and for 350° and 375° at other lower initial pressures ; e. g., $P_0=13$ cm and 8 cm of Hg.

All the plots of Δp vs log t are linear with discontinuities with one or two breaks. But by choosing a suitable value of 'k' they could be linearised with the exception of two expts. The plots of α vs 1/T do not show any regular variation with $P_0=17$ cm. α vs 1/T plot is parabolic whereas with $P_0=27.2$ cm the plot shows a maximum at 325°. So a change in the nature of active sites[12] occur at 325°, at least for $P_0=27.2$ cm of Hg. Adsorption isotherm studies indicate the adsorption to be highest at 325° and was further supported by an endothermic peak in the DTA thermogram at 325° proving this to be a characteristic temperature of the catalyst in respect of its behaviour as an oxidation catalyst (for oxygen chemisorption).

The initial massive adsorption, a^*, increases with temperature for $P_0=17$ cm, but for $P_0=27.2$ cm at 375° there is some deviation in the trend of increase shown in the plot of log a^* vs 1/T. Activation energy was calculated using a^* (a_1) with the help of the equation :

$$\log\,(\text{rate})=\log\left(\frac{d\,\Delta p}{dt}\right)=\log a-\frac{\alpha}{2.303}\times\Delta p_0 \quad \ldots (2)$$

It has been found to be 4.37 K cal/mole for $P_0=17$ cm and 9.14 K cal/mole for $P_0=27$ cm. Plot of

TABLE 5—ISOSTERIC HEAT OF ADSORPTION (ΔH) CALCULATED FROM THE ISOTHERMS

300°-350°		300°-375°		325°-350°		325°-375°		350°-375°	
V(cc)	(K. Cal) ΔH	V(cc)	(K. Cal) ΔH	V(cc)	(K. Cal) ΔH	V(cc)	(K. Cal) ΔH	V(cc)	(K. Cal) ΔH
3.0	2.48	3.0	17.80	3.0	15.96	3.0	33.8	3 0	53 08
3.5	3.46	3.5	17 60	3.5	15.75	3.5	31.99	3.5	49 55
4.0	3.80	4.0	16.36	4 0	14.90	4 0	29 10	4 0	44 38
4 5	3.13	4 5	15 40	4 5	14 19	4.5	27 90	4 5	42 73
5.0	3.07	5 0	15.44	5.0	14.70	5.0	28.47	5.0	43.36
5.5	3 07	5.5	14.89	5.5	15.67	5 5	28.06	5.5	41.02
6.0	2 58	6.0	14.09	6 0	17.87	6.0	28 56	6.0	40.11

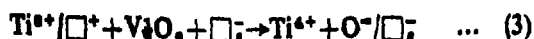
activation energy (E) vs coverage (Δ_p) is not linear, but shows a maximum around Δ_p=0.03 cm. The parameter 't_0' which according to Low[13] indicates the time at which slow adsorption starts, has been found to be irregular in the present case and is probably of minor importance.

It is rather certain that during the preparation of the sample V_2O_5-Ti_2O_3, Ti^{3+} present would have been oxidized to Ti^{4+} with simultaneous conversion of V^{5+} to V^{4+} and possibly to other lower valent states. But from the study of the states of TiO_2 heated in vacuum[5], it has been shown that it is converted to an non-stoichiometric compound of the type $Ti_{1-x}O_{2-y}$ (titanium and oxygen entering gas phase) and Ti^{3+} is formed. X-ray analysis data show two strong lines with those of TiO_2 (Ti^{4+}) supporting our view.

Magnetic susceptibility measurements give μ_{eff} to be 3.67 B.M. as against 3.89 indicating the presence of 3 unpaired electrons.

After pretreatment and evacuation of catalyst, probable sites for attach may be Ti^{3+}, V^{4+}, V^{3+} and other lower valent states of vanadium. Oxygen may be adsorbed on these sites either as O^-, O_2^- or $O^=$ species. But at high temperatures, the formation of the species O_2^- [14] is ruled out owing to the fact that physically adsorbed oxygen may be a weakly chemisorbed species like O_2^- [14]. From the table of heat of adsorption for the temperature range 350°-375°, ΔH varies from 53-40 K cal. It is highly probable that at this temperature oxygen will be adsorbed as $O^=$, forming higher oxides. It has also been observed that after the chemisorption of oxygen, the chemisorption of hydrogen on the same specimen is higher indicating the likely adsorption of $O^=$ species.

From the X-ray spectroscopic data of the sample after oxygen chemisorption studies, a very strong line has been found to coincide with a very strong line of TiO_2 (Rutile) indicating the formation of the higher oxide. The probable mode of adsorption may be :

$$Ti^{3+}/\square^+ + V_2^{4}O_4 + \square_s^- \rightarrow Ti^{4+} + O^-/\square_s^- \quad \dots (3)$$

The conductivity of the pelletted sample was measured both in vacuum and in oxygen atmosphere. The conductivity in oxygen atmosphere at 300° increased in the first minute from 27.02×10^{-4} ohm^{-1} cm^{-1} to 78.15×10^{-4} ohm^{-1} cm^{-1} and then decreased continuously. The reason for this increase is probably the adsorption of O^- species, because O^- species have a tendency to donate one electron to the conduction band forming uncharged 'O' species. This has also been proved by the work of Morrison[15]. Adsorption in the later stage may proceed as

$$O_{ads} + e + \square_s^- \rightarrow O^-/\square_s^- \quad \dots (4)$$

leading to a decrease in the conductance. The O^- species may accept an electron from the F centre or from the conduction band to form $O^=$ species. This $O^=$ may fill up the lattice vacancies leading to the formation of TiO_2 and higher oxides of vanadium. As has been stated, the adsorption of oxygen directly as $O^=$ is also not unlikely. But whatever may be the case, it is almost certain that excess of $O^=$ are created after oxygen adsorption.

Conclusion :

From previous work[4] the activity of V_2O_5 has been attributed to the joint presence of V_2O_5 and $V_2O_{4.34}$ involving a dynamic equilibrium between V_2O_5 like structure and $V_2O_{4.34}$ like structure. Some recent work on the oxidation involving V_2O_5[16] suggest that the presence of different lower valent states are responsible for catalytic reactions. We have deliberately added Ti_2O_3, introducing more of defect centres and our work seem to coroborate this view. From the work of Bhattacharyya *et al*[17] and our work[6], the adsorption does not proceed at low temperatures, pressures and small amounts of sample. Comparison of the results show that the defects introduced play a definite role in the adsorption of oxygen facilitating oxidation reactions.

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Complexation of Salicylanilide with Some Metal Ions of Biological Interest

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In order to examine complexation as a possible mode of action of some fungicides, the complexation of salicylanilide with a few metal ions of biological interest, such as, Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Zr(IV), La(III) and Th(IV), has been studied potentiometrically using Calvin-Bjerrum titration technique as employed by Irving and Rossotti. Protonation constant of the ligand and stability constants of the respective metal complexes have been determined at constant temperature (25°) and ionic strength (0.1 *M*, KNO_3) in 70% (v/v) dioxan-water medium. Complexes of salicylanilide with Fe(III), Ni(II) and Cu(II) have also been prepared and characterized on the basis of elemental analysis and ir spectral data. A possible mechanism of action of this fungicide has been discussed.

THE activity of various metal ions in biological systems has been explained on the basis of different complexed species formed in the living organisms[1,2]. Metal ions are found in several fungi[3] and are reported to play important role in different enzymatic reactions. A survey of literature reveals that the role of metal ions in fungicidal activity is rather unexplored. Salicylanilide is a potential fungicide[4] and its mode of action has been investigated only to the extent of some physiological[3,4] changes occurring in fungi but the structural features have not been considered. To explore this aspect of fungicidal activity, complexation of salicylanilide with some metal ions of biological interest, such as, Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Zr(IV), La(III) and Th(IV) has been investigated in solution potentiometrically. The complexes of Fe(III), Ni(II) and Cu(II) with salicylanilide have also been isolated in solid state and studied to establish the site of interaction.

Experimental

Materials: All the metal nitrates used were of AR grade and their solutions were prepared in carbonate free double distilled water. Salicylanilide was obtained from Fluka A.G. and weighed quantity of the anilide was dissolved in 70% (v/v) dioxan-water medium.

Potentiometric measurements: A Beckman *p*H meter with glass calomel electrode assembly was used for *p*H measurements. The following mixtures were prepared for each metal and titrated against standard alkali using Bjerrum-Calvin *p*H-titration technique:

(a) 5 ml KNO_3 (1.0 *M*)+10 ml HNO_3 (0.01 *M*),

(b) 5 ml KNO_3 (1.0 *M*)+10 ml HNO_3 (0.01 *M*) +10 ml ligand (0.01 *M*),

(c) 5 ml KNO_3 (1.0 *M*)+10 ml HNO_3 (0.01 *M*) +10 ml ligand (0.01 *M*)+2 ml metal nitrate (0.01 *M*).

Total volume of each system was kept at 50 ml by appropriate addition of water and dioxan. Representative potentiometric titration curves are shown in Fig. 1
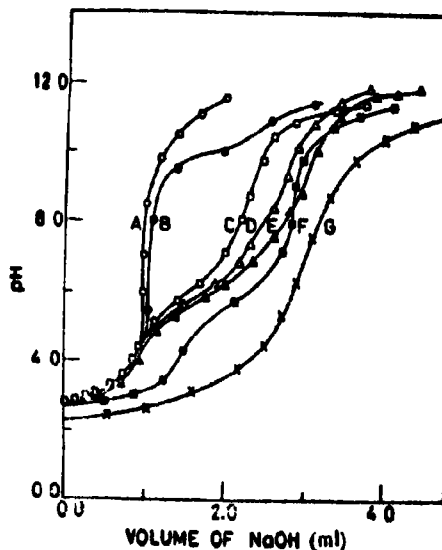
Fig. 1. Potentiometric titration curves A: Free acid; B: Ligand (L); C: Cu(II)-L; D: Ni(II)-L; E: Co(II)-L; F: Fe(III)-L; G: Th (IV)-L.

Protonation constant: The average number of protons associated with a ligand, $\bar{n}_A$, was calculated using the formula of Irving and Rossotti[5]

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$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^0 + E^0)}{(V_0 + V_1) T_L^0}$$

where V_1 and V_2 denote the volume of alkali required to reach the same pH in titrations of HNO_3 and ligand, respectively, T_L^0 the total concentration of ligand, Y the total number of dissociable protons attached to a ligand, N^0 the normality of alkali, V_0 total volume of mixture and E^0 the initial concentration of free acid. Proton ligand formation curve, obtained by plotting $\bar{n}_A$ values against pH values, was utilized to evaluate the protonation constant employing various computational methods[4].

Metal-ligand stability constants: The average number of ligand associated with a metal ion, $\bar{n}$, and the free ligand exponent, pL, were calculated by using equations,

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V_0 + V_1)\, \bar{n}_A\, T_M^0}$$

and

$$pL = \log_{10}\left[\frac{\beta\left(\frac{1}{\text{Antilog}\ \beta}\right)^n}{T_L^0 - \bar{n}\, T_M^0} \cdot \frac{(V_0 + V_3)}{V_0}\right]$$

Metal ligand formation curves (Fig. 2) obtained by plotting $\bar{n}$ against pL were utilized to calculate successive stability constants of metal complexes using Rossotti's computational techniques[5].

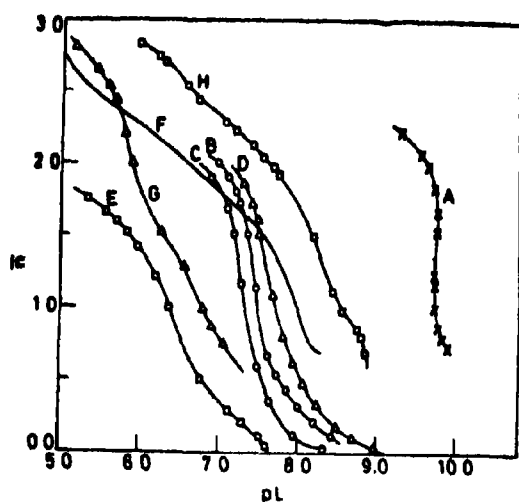



Fig. 2 Metal ligand formation curves. A: Fe(III)-L; B: Co(II)-L, C: Ni(II)-L; D: Cu(II)-L; E: Zn(II)-L, F: Zr(IV)-L, G: La(III)-L; H: Th(IV)-L.

General method of isolation of complexes: Equimolar amounts of salicylanilide and nickel or cupric nitrate were dissolved in ethanol separately. The solution of salicylanilide was neutralized with equimolar solution of NaOH in ethanol and added to excess of metal nitrate solution with constant stirring. The precipitate was filtered, washed with hot benzene and dried. The Fe(III) complex was isolated by adding neutral solution of salicylanilide into excess ferric chloride solution in ethanol. The mixture was filtered and the filtrate was evaporated. Residue was recrystallized from ethanol to give Fe(III) complex. Some analytical data of these complexes are given in Table 1.

TABLE 1—SOME ANALYTICAL DATA OF THE METAL COMPLEXES OF SALICYLANILIDE

Complex	Colour	% Found (Calcd.)			
		C	H	N	M
$Fe[C_{13}H_{11}O_2N]_3$	Violet	67.50 (67.30)	4.23 (4.33)	6.57 (6.69)	7.96 (8.09)
$Ni[C_{13}H_{11}O_2N]_2$	Green	64.27 (64.40)	4.02 (4.14)	5.71 (5.80)	12.28 (12.16)
$Cu[C_{13}H_{11}O_2N]_2$	Olive green	63.89 (64.0)	4.0 (4.10)	5.62 (5.74)	13.09 (13.02)

Results and Discussion

Protonation constant (Table 2) of salicylanilide was obtained by plotting $\bar{n}_A$ against corresponding pH values and interpolating at half $\bar{n}_A$ value of the curve. Examination of representative titration curves (Fig. 1) shows that metal titration curves are well separated from the ligand titration curve. Metal-ligand formation curves for Co(II), Ni(II), Cu(II) and Zn(II) (Fig. 2, curves B, C, D and E, respectively) are complete at both ends. Hence values of log k_1 and log k_2 were obtained directly by interpolating at $\bar{n}$=0.5 and 1.5, respectively. Due to symmetry of formation curves, it was also possible to determine the stability constant data by 'mid point' method. Formation curves of Fe(III), Zr(IV), La(III) and Th(IV) (Fig. 2, curves A, F, G and H, respectively) are, however, incomplete in lower half portions and thus the values of log k_2 and log k_3 were obtained at $\bar{n}$=1.5 and 2.5, respectively, while those of log k_1 were obtained using the equation,

$$\log k_1 . k_2 = 2pL \ (\text{at}\ \bar{n} = 1.0)$$

TABLE 2—STABILITY CONSTANTS OF THE COMPLEXES OF SOME METAL IONS WITH SALICYLANILIDE; μ = 0.1 M (KNO_3); t = 25° (PROTONATION CONSTANT OF SALICYLANILIDE, pKa = 9 68)

Metal Ion	log k_1	log k_2	log k_3	log β
Fe(III)	9 84	9.76	–	19.60
Co(II)	7.80	7.15	–	14.95
Ni(II)	7 70	7.58	–	15.28
Cu(II)	8 08	7.56	–	15.64
Zn(II)	6 78	5 84	–	12.62
Zr(IV)	8 50	7.58	5.30	21.38
La(III)	7 40	6 28	5.60	19.28
Th(IV)	9 00	8.20	6 65	23.85

The calculated values of log k_1, log k_2 and log k_3, alongwith the protonation constant (pKa) of salicylanilide have been reported in Table 2. The log k_4 values for Zr(IV) and Th(IV) could not be calculated due to limited accuracy of $\bar{n}$ values. The general order of overall stability constant values have been found to be: Th(IV) > Zr(IV) > Fe(III) > La(III) > Cu(II) > Ni(II) > Co(II) > Zn(II) in which Fe(III), Cu(II), Ni(II) and Co(II) are according to Irving-Williams' sequence[6].

In the absence of metal ion hydrolysis, proton release on complexation can be only from the ligand. If the solutions are not highly alkaline, the protonation equilibrium investigated is $HL \rightleftharpoons H^{+} + L^{-}$ and complex formation takes place through the displacement of phenolic hydrogen.

The analysis of representative species distribution curves of Cu(II) complex (Fig. 3) reveals that the concentration of species CuL^{+} increases rapidly, attains a limiting value ($\simeq$50%) at a *p*H of 5 and decreases beyond this *p*H, thereby increasing the concentration of CuL_2. It has been noted that at higher *p*H values, almost all Cu(II) complexes with salicylanilide in the form of CuL_2 ($\simeq$100%). Similar observations have been obtained with systems of salicylanilide with other metal ions where substantial decrease in the concentrations of ML^{+} species increases the concentrations of ML_2 species. The maximum concentrations of ML^{+} type of complexes for Co(II), Ni(II), Zn(II), Zr(IV), La(III) and Th(IV), were found to be 44, 48, 59, 58, 64 and 54%, respectively, whereas for ML_2 type complexes were found to be 95, 95, 96, 87, 50 and 73%, respectively. The concentrations of ML_2 type complexes of Zr(IV), La(III) and Th(IV) were observed to attain limiting values at 93, 95 and 92%, respectively. In all the cases, the concentration of each species tends to approach a limiting value and total concentration of metal, present in various species, was found to be nearly 100% at any *p*H.

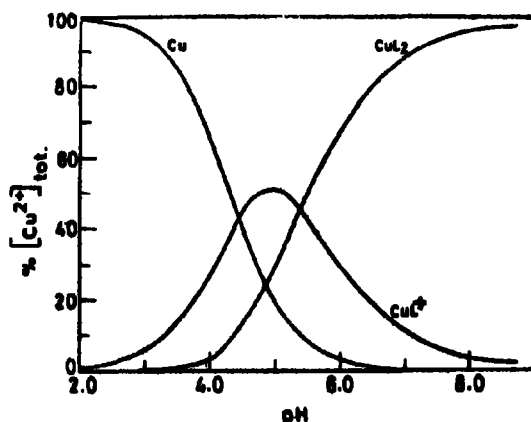
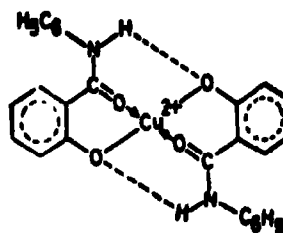



Fig. 3. Species distribution curves [given as the percentage of total Cu(II) present] of several species present in binary system of Cu(II) and salicylanilide ($C_M = 1 \times 10^{-3} M$ and $C_L = 2 \times 10^{-3} M$).

Nature of reaction leading to complex formation : There are three possible binding sites in salicylanilide, two in amide group (one through its oxygen and the other through the nitrogen atom) and the third one through the phenolate oxygen. The negative shift observed in the N-H stretching frequency of ligand from 3270 cm^{-1} to 3250, 3255 and 3260 cm^{-1} for Fe(III), Ni(II) and Cu(II) complexes, respectively, has been interpreted as due to intramolecular hydrogen bonding between N-H group and phenolate oxygen bonded to metal ion and not due to bonding with metal ion as the potentiometric determination of dissociation constant of salicylanilide has provided only one protonation constant (Table 2) due to phenolic group. Further, lowering of $\nu C{=}O$ of salicylanilide from 1620 cm^{-1} to 1600, 1600 and 1585 cm^{-1} for Fe(III), Ni(II) and Cu(II) complexes, respectively, provides substantial evidence that the metal ions are coordinated through oxygen atom of amide group (Structure 1). These results are further supported from the work of Rao[7], Bilger and Pechmeze[8] and Pannu and Chopra[9] on similar systems.

Structure-1

On the basis of present investigation, it has been observed that salicylanilide is capable of forming stable complexes with the metal ions which are found in conjugation with the enzymes where these metal ions may establish 'some sort of equilibrium' with fungicides. Thus, the growth inhibition of fungi may be due to removal of a metal ion from the enzyme to form its complex with fungicide, thereby disturbing the biological activity. Similar observation on dithiocarbamates has been recorded by Gokosyr[10], Smale[11] and Kaars Sijpesteyn *et al*[12]. A detailed investigation of this mechanism is in progress.

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Melting Behaviour of Some Pure N-Acyl Amino Acids and Peptides

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Fifty three tlc pure N-acyl amino acids were synthesized by Schotten-Baumann reaction from glc pure odd and even chain fatty acids and chromatographically homogeneous amino acids and a few N-acyl peptides were prepared through the carboxylic carbonic anhydride intermediates The melting points are reported and discussed.

N-ACYL amino acids and peptides are finding use as surfactants and surfactant intermediates[1]. The melting points of several even chain fatty acids derivatives were reported by earlier workers[9-18] and the m.p.s of only N-acylsarcosines of odd and even chain fatty acids were reported by Jungermann *et al*[18]. Systematic data on the effect of structure of these compounds on their melting behaviour are not available, and hence this investigation. The surfactant properties of the sodium salts of these acids are being communicated separately.

Experimental

Preparation of glc pure fatty acids : GLC pure even chain fatty acids from decanoic to octadecanoic were prepared from commercially available fatty acids by ester fractionation and crystallisation technique[2]. Hendecanoic acid was prepared from laboratory hydrogenated methyl hendecanoate. Tri, penta and heptadecanoic acids were prepared through the nitrile route[3,4] from even chain fatty alcohols obtained by sodium reduction of the corresponding glc pure fatty acid esters.

Preparation of N-acyl amino acids : Fatty acid chlorides were prepared using thionyl chloride according to the procedure of Bauer[5] and further purified by vacuum distillation. These were condensed by Schotten-Baumann reaction with chromatographically homogeneous amino acids, viz, glycine (gly), DL-alanine (ala), DL-valine (val), L-leucine (leu), L-aspartic acid (asp) and L-lysine (lys). Pure sarcosine (sar), ε-amino caproic acid and ω-amino hendecanoic acid derivatives were also prepared to study the effect of structure on melting behaviour.

In general, appropriate acid chloride was added dropwise, with constant stirring, to an aqueous solution of sodium salt of amino acid (taken in 20% molar excess except for lysines where 3 moles of acid chloride per mole of amino acid was used) while maintaining the temperature at 45±5° ; the *p*H of the reaction mixture being maintained at 10±0.5 by careful addition of 10% aqueous NaOH solution. The stirring was continued at the same temperature for 1 hr more after the addition was over, and the product was acidulated with 30% sulphuric acid. The separated N-acyl amino acid was taken in an appropriate solvent, washed free of mineral acid and repeatedly crystallised from appropriate solvent till completely free from fatty acids as adjudged by tlc.

Toluene was found to be suitable for extraction of N-acyl glycines, -alanines and -lysines, while hexane gave good results for -valines and -leucines ; 95% ethanol was found to be good solvent for crystallisation for all these. For the N-acyl sarcosines, ethyl ether was used as extraction solvent and hexane as solvent for purification by crystallisation.

N-acyl aspartates were prepared in aqueous acetone according to Takehara *et al*[6] instead of plain aqueous media as for others.

Preparation of N-acyl peptides: N-acyl glycyl glycines were prepared from 2,5-diketopiperazine[7] and acid chloride according to Koebner[8]. The others were prepared by an evolved procedure through the carboxylic carbonic anhydrides. The details of preparation of hendecanoyl glycyl alanine are as follows.

N-hendecanoyl glycine was taken in tetrahydrofuran, and to it was added triethylamine in 20% molar excess ; the contents were cooled to -5° while stirring and ethyl chloroformate (again 20% molar excess) was added drop by drop while maintaining the temperature at 5°. After completion of addition, the mixture was stirred for another 10 min followed by addition of 10% aqueous solution of sodium salt of DL-alanine (20% molar excess). The contents were then allowed to reach room temperature, further stirred for 30 min and acidified to a *p*H of 3 0. The precipitate formed was washed till free of mineral acid, and the N-hendecanoyl glycyl alanine

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TABLE 1—MELTING POINTS OF PURE N-ACYL AMINO ACIDS

No. of atoms C-atoms in parent acid and its m.p. (in brackets)	Melting points, °C. (Figures in brackets are earlier reported values)						
	Amino acid						
	Glycine	DL-alanine	Sarcosine	DL-valine	L-leucine	L-aspartic acid	L-lysine
10 (36.5)	113	97	36.5 (37.5-38.5)[18]	90	109 (109-109.5)[18]	103	113
11 (28.0)	114	102	48.5 (49.4-50.2)[18]	80.5	108 (108-109)[19]	–	113
12 (44.1)	117 (117-118)[6,10]	104 (95-96)[17] (103-105)[9,10,18]	45.6 (45.2-45.8)[18]	92 (91-92)[14]	107 (106-107)[14]	109 (107-109)[9]	117
13 (41.6)	118	107	58.6 (59.8-60)[18]	82.6	103	–	–
14 (54.3)	121 (121-122)[9]	109	52.0 (51-52)[18]	97.0	101	115	119
16 (62.8)	123* (121)[10]	114 (116-117)[6] (106)[10]	60.0 (65.5-66.5)[18]	99.0 (95-98.5)[15]	91.0 (88-89)[16]	118	122 (121-122)[16]
17 (61.1)	124	114	71.4 (71.4-71.9)[18]	83.5	87.3	–	–
18 (69.5)	127 (125-127)[11] (123)[13]	116 (115-117)[11] (108-110)[13]	71.5 (65.6-66.5)[13] (71.8-72)[18]	100	65.0	119	–

* m.p.s of linear N-acyl amino acids having a total 18 C-atoms are as follows :

Pentadecanoyl-β-alanine, 115° ; dodecanoyl-ε-amino caproic acid, 86° ; heptadecanoyl-11-amino hendecanoic acid, 98°.

was crystallized from tetrahydrofuran repeatedly till a product of constant m.p. was obtained.

N-hendecanoyl alanyl glycine was similarly prepared from N-hendecanoyl alanine and sodium glycinate ; so also N-acyl glycyl glycyl glycines were prepared from N-acyl glycines with sodium salt of glycyl glycine, and condensation of N-hexadecanoyl glycyl glycine with sodium salt of glycyl glycine gave N-hexadecanoyl glycyl glycyl glycyl glycine.

Determination of melting points : All the products were taken in closed capillary and their melting points were determined by the usual method.

Discussion

The determined acid values (not reported here) and also the determined nitrogen content of the peptides agree closely with theoretical values confirming the purity of products as tested by tlc. The m.p.s of thirty N-acyl amino acids are being reported for the first time ; the m.p.s of others are closer to the values reported earlier with a few exceptions (Table 1). The m.p.s reported by Spivack and Kroll[13] for stearic acid derivatives of glycine (123°), alanine (110°) and sarcosine (66.5°) are consistently lower than the present values (127, 116 and 71.5°, respectively). The present values, however, are nearer to the values reported by Fieser *et al*[11] (stearoyl glycine 127° and stearoyl alanine 117°) and Jungermann *et al*[18] (stearoyl sarcosine, 72°). Koebner[8] reported a m.p. of 172° for hexadecanoyl glycyl glycine which is lower than the value (179°) obtained in the present study by 7° ; the m.p.s of the other acyl peptides are being reported for the first time (Table 2).

TABLE 2—MELTING POINTS OF N-ACYL PEPTIDES

Peptide	Melting point, °C	
	Acid	
	Hendecanoic	Hexadecanoic
gly. glycine	182	179*
gly. alanine	168	–
ala. glycine	141	–
gly. gly. glycine	211	208
gly. gly. gly. glycine	–	229

* Reported m. p. is 172° ; soon after melting all the compounds get darkened due to decomposition.

The effect of increasing the acyl chain length on m.p. of homologues varied from series to series. The N-acylated sarcosine series resembles the fatty acid series in alternation of m.p.s of odd and even

chain compounds, but the alternations are opposite. Alternation is apparent (Fig. 1) in valine series also, but here it is like that for fattty acids, i.e. the m.p. of even acyl chain compounds is higher than that of the odd acyl chain compounds having one carbon atom more. If the odd and even acyl chain compounds of valine and sarcosine are treated as separate series, the m.p.s increase as the series are ascended as in the case of fatty acids. Alternation is absent in the series of glycines, alanines, lysines and leucines; in the case of the first three series, m.p.s increase as the series are ascended, but they decrease in the case of N-acyl leucines, indicating that shorter acyl chain derivatives are packed more closely in solid state. This differential melting behaviour of homologues belonging to different series is, no doubt, due to the differences in structure of the amino acid present.
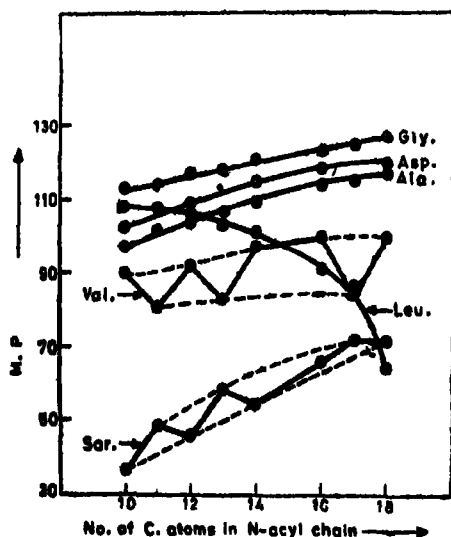
Fig. 1. Relations of No. of C-atoms in the N-acyl amino acids and their melting points.
(gly, glycines; asp, aspartates; ala, alanines; val, valines; sar, sarcosines and leu, leucines)

Compared to parent fatty acids, N-acyl amino acids have higher m.p., the exceptions being decanoyl and tetradecanoyl sarcosines and N-octadecanoyl leucine (Table 1). The difference in m.p. of lower and higher homologues for the N-acyl amino acids is not much as compared to that of fatty acids except for sarcosine and leucine series which perhaps can again be attributed to structural differences of amino acids.

DL-alanines (α-methyl glycines) do not show alternation in melting behaviour while the sarcosines (N-methyl glycines) do for any given acyl chain; the compounds in former series have higher m.p. than those of the latter even though their molecular weights are same.

The magnitude of substituent group at the α-position of the glycines also plays an important role in the melting behaviour. For any given acyl chain, alanines (α-methyl glycines) have higher m.p. than valines (α-isopropyl glycines) which in turn melt at a higher temperature than leucines (α-isobutyl glycines). Further, as has already been mentioned, as the molecular weight is progressively increased, m.p. increases in alanine series, alternates in valine series and decreases in leucine series. Aspartates (decarboxylates) have m.p.s between those of the corresponding glycines and alanines. All these indicate that the substituent group plays an important role on the intramolecular interaction forces exerted by acyl chains, intermediate amido groups and terminal carboxyl groups of the compounds altering the packing of molecules in solid state. Two long acyl chains as in lysines (diacylated lysines) make the compounds behave like the corresponding glycines. Even though the molecular weights of compounds of the former series are nearly twice of the corresponding ones in the latter, their m.p.s are very close and in two cases they coincide (Table 1). That the position of the intermediate amido group also has a significant effect on the molecular packing in solid state is clear from a comparison of the melting points of four linear N-acyl amino acids having a molecular weight of 313 (having a total of 18 carbon atoms). N-hexadecanoyl glycine (m.p. 123°) has higher m.p. than N-penadecanoyl alanine (m.p. 115°) which in turn melts higher than N-heptanoyl amino hendecanoic acid (m.p. 98°). These three compounds have 1, 2 and 10 methylene groups between the terminal carboxyl group and nitrogen atom. This indicates that m.p. decreases as the amido group moves away from the carboxyl group in the molecule but again increases when it is nearer to the other end of the molecule (N-dodecanoyl-amino caproic acid melts at 86°).

Incorporating glycine groups increases the m.p. The m.p. of N-hexadecanoyl glycine (123°) is almost twice that of palmitic acid (62.8°). Presence of additional amido groups in the former increases the m.p. further but not linearly (m.p s of N-hexadecanoyl glycyl glycine, -glycyl glycyl glycine, -glycyl glycyl glycyl glycine are 179, 208 and 229°, respectively). Here also, like the leucines and unlike other acyl amino acid series, the hendecanoyl derivatives have higher m.p. than those of their corresponding higher homologues (hexadecanoyl derivatives) indicating the combined effect of acyl chain length and the polar part of the molecule on the melting behaviour.

In the peptides also, presence of substituted group (methyl) decreases the m.p. (Table 2); N-hendecanoyl glycyl glycine melts at a temperature (m.p. 182°) higher than that for hendecanoyl glycyl alanine (m.p. 168°) and hendecanoyl alanyl glycine (m.p. 141°). It is interesting to note that the sequence of amino acids in peptides has a profound effect on the molecular packing.

The length of the acyl chain as well as the structure of amino acid present in the compounds play an important role in the melting behaviour and in addition to these, the number and sequence of amino acids present have a profound effect on the molecular packing of N-acyl peptides.

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Properties of Pure Sodium Soaps of Saturated Fatty Acids

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Pure sodium salts of odd and even chain fatty acids (C_7 to C_{19}) were prepared and their properties and performance characteristics were evaluated.

The odd and even chain fatty acid soaps, in water, appear to behave as two separate surfactant series with respect to their solubility and critical micelle concentration; the higher soaps behave somewhat anomalously perhaps due to coiling of longer hydrophobic chains in aqueous solutions, while the lower soaps having very high CMC are ineffective as surfactants at the usual concentrations.

MANY reports have appeared on the properties of sodium soaps of fatty acids having even number of C-atoms originating from natural fatty oils[1]. Reports on some properties of odd chain fatty acid soaps have started appearing only recently[2,3]. Due to differences in test conditions of different workers, it is not possible to compare the properties of odd and even chain fatty acid salts at any given temperature. A detailed comparative study of the properties of sodium salts of fatty acids, from heptanoic to nonadecanoic, was, therefore, taken up.

Experimental

Preparation of sodium salts of pure fatty acids: Four odd chain saturated fatty acids, viz. tri-, penta-, hepta- and nonadecanoic acids, were synthesized by the nitrile route[4]. GLC-pure methyl esters of even chain fatty acids were reduced to fatty alcohols by the sodium reduction method, which were then converted to iodides from which nitriles were prepared. The nitriles were hydrolysed by alcoholic NaOH and the soaps obtained were freed from unreacted impurities by repeated crystallizations from alcohol. All the other pure acids were prepared from the commercial fatty acids by the usual ester fractionation technique and, wherever necessary, by hydrogenation and/or solvent crystallization. The melting points of the glc and tlc pure fatty acids (purity of over 99.9%) agree closely with earlier reported values[5,6,7]. The relationship of m p. with the number of C-atoms in the acids is shown in Fig. 1a. The pure fatty acids taken in alcohol were neutralised with alcoholic sodium hydroxide and the soaps were purified by recrystallization from alcohol, dried and stored in a desiccator.

Evaluation of the properties and performance characteristics of soaps in water: The pure soaps were evaluated by the methods described earlier[8-10]. The temperature at which 1% aqueous soap solution becomes clear (K. P.) and the temperature at which clouding occurs while gradually cooling the clear solutions (C. P.) are given in Table 1 and represented in Fig. 1 (b and c). pH of 0.25% aqueous solutions, interfacial tension (I. T.) of 0.1% solutions against
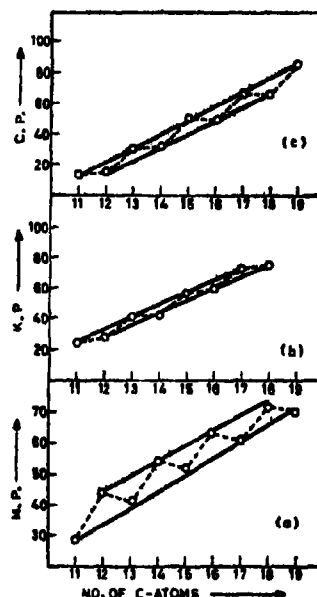
Fig 1. Relationship of No. of C-atoms with (a) m.p. of fatty acids, (b) K.P. of fatty acid soaps and (c) C. P. of fatty acid soaps.

toluene and the minimum surface tension values (S. T.) attained by the soap solutions are given in Table 1. Critical micelle concentrations (CMC) of the soaps obtained by graphical methods from the S. T. and conductivity data of solutions varying in concentration are also given in Table 1. The relationship of log molar CMC (by conductivity method) and the number of C-atoms in soap is

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shown in Fig. 2. All the properties and performance characteristics of the soaps were evaluated, at 60°, in distilled water except the S. T. determinations which were in presence of added sodium meta silicate (5% based on soap).
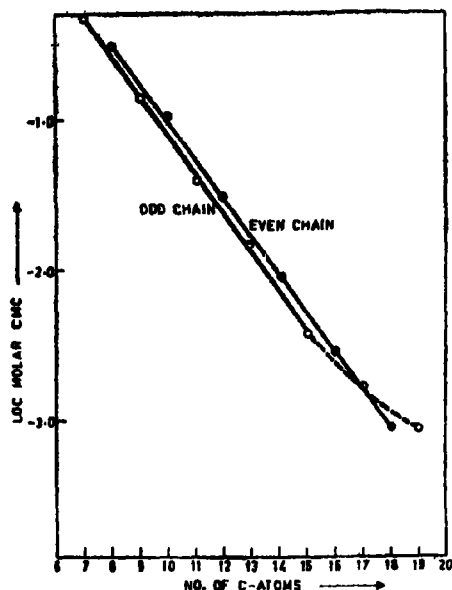
Fig. 2. Relationship of log molar CMC of sodium salts and No. of C-atoms present.

of one C-atom to an even chain fatty acid soap (upto palmitate) means effective increase in the chain length by about 1.5 C-atoms from the solubility considerations, while for the odd chain soaps it means reducing effective chain length by less than one C-atom (about 0.5).

The *p*H of 0 25% solutions of different soaps progressively increases with increasing chain length (7.2 to 10.3 for decanoate to nonadecanoate) indicating the tendency of higher soaps for greater hydrolysis in distilled water. The same trend is observed (results not given) at different concentrations studied and also at 30°. The calculated maximum percentage hydrolysis for C_7 and C_{19} soaps, at 60°, are $115 2\times10^{-4}$ and 27.4×10^{-4}, respectively, and the other soaps have values in-between, but the concentrations at which maximum percentage hydrolysis occurs differ for different soaps.

Sodium myristate is the best amongst the soaps in respect of I. T. lowering power. The ability, however, decreases when the series is either ascended or descended indicating the need for a proper HLB.

The need for optimum HLB is also apparent in the various performance characteristics of the soaps studied at 60° (but not reported in the table). In the wetting tests (canvas disc method[10] using 0.1% soap solutions) sodium laurate was found to be the best (wetting time of 31 sec) followed by hendecanoate (38 sec) and tridecanoate (60 sec),

TABLE 1—PROPERTIES OF AQUEOUS SOAP SOLUTIONS AT 60°

No. of Carbon atoms in soap	K. P. °C	C. P. °C	*p*H of 0.25% solution	I. T. of 0.1% soln. (dynes/cm)	Min. S. T. (dynes/cm)	CMC, m moles/l S. T. method	CMC, m moles/l Conductivity method
7	*	*	–	32	40	461	467
8	*	*	–	33	39	301	301
9	*	*	–	32	36	139	136
10	*	*	7.2	31	34	103	106
11	24.3	10.7	7.6	29	34	40	38
12	28.1	16.0	7.6	28	31	30	31
13	41.2	31.4	8.6	26	28	13	12
14	43.9	35.3	9.1	20	27	8	9
15	57.4	50.0	9.4	27	24	3.6	3.8
16	61.3	54.3	9.8	30	22	2.7	2.9
17	73.2	66.8	10.0	31	26	1.7	1.7
18	75.5	68.0	10.2	33	27	0.8	0.9
19	83.6	77.2	10.3	34	36	0.9	0.9

* Clear at 0°

Results and Discussion

The solubility of the soaps progressively decreases with the increase in their molecular weight as shown by the progressive changes of K. P. and C. P. (Table 1). However, when K. P. (Fig. 1b) and C. P. (Fig. 1c) are plotted against the number of C-atoms present in the soap, the points for odd and even chain acid soaps fall on two separate lines, as for the m.p. of fatty acids (Fig. 1a). The K. P. and C. P. lines of odd chain fatty acid salts are above those of the even chain, whereas the m.p. line of the odd chain fatty acids is below that of the even chain acids. The figure indicates that the addition

while the rest of the soaps are poor wetting agents under the test conditions. The 0.25% solutions of salts from heptanoate to decanoate do not foam in the Ross-Miles pour foam test[11] at 60° and hendecanoate gives poor unstable foam (only 55 mm). The other soaps, laurate to palmitate in distilled water, foam better than sodium lauryl alcohol sulphate (NaLAS) but again foaming ability decreases as the molecular weight increases. However, as adjudged by the foam height after 5 min, the stability of foam formed increases as the molecular weight increases. The detersive power (in the soiled cotton fabric-washing tests using Tergo-o-Meter[9])

of higher soaps (tetradecanoate and above) is better than NaLAS, while the lower ones are poorer. The detergency of 0.25% soap solutions from heptanoate to hendecanoate are only 10-12% of that of sodium stearate. In general, the medium chain fatty acid soaps showed poor performance characteristics and are ineffective as surfactants at the tested concentrations (normally employed).

In all cases, the S. T. decreases with increase in the concentration till around the CMC of the soap, and the minimum values obtained are given in Table 1. The S. T. lowering power (effectiveness) is maximum for palmitate and pentadecanoate, amongst the soaps of even and odd series, respectively. The effectiveness decreases if the chain length is either increased or decreased, showing the need for optimum HLB for effective S. T. reduction.

CMC values of the soaps in distilled water obtained by the conductivity method are close to those obtained by the S. T. method (Table 1). They are also nearer to the values obtained by the pinacyanol chloride dye method (not reported).

The short chain fatty acid soaps (caprate and below) will be effective only at a very high concentration (as CMC of caprate is 2% by weight) which is not encountered in actual usage. The CMC, in general, decreases with increase in the chain length till stearate and there is no perceptible effect by further increase in the chain length by one more -CH_2 group. When log molar CMC is plotted against the number of C-atoms in the soap molecules, a very interesting picture emerges (Fig. 2). Two separate straight lines are obtained for odd and even chain acid soaps upto palmitate, indicating that the odd and even chain soaps behave as two separate surfactant series. It is apparent from Fig. 2 that increasing the acyl chain of odd chain fatty acid soap by one CH_2 group (next higher even chain fatty acid soap) appears to increasing the effective chain length (ECL) by only 0.6 CH_2 group till palmitate. Conversely, increase in one CH_2 group in even chain fatty acid soap means increase in ECL by 1.4 CH_2 group. The anomalous solubility behaviour and CMC data may be due to the difference in intermolecular attraction forces between the acyl chains having odd and even number of C-atoms and/or due to the difference in arrangement of soap molecules in micelles. The CMC of the heptadecanoate falls on the line of even chain fatty acid soaps while nonadecanoate has CMC which is the same as that of the stearate. This behaviour of the higher soaps in water may be due to the coiling tendency of their long hydrophobic acyl chains as postulated by Mukerjee[12].

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Synthesis and Studies of Some New Phthal-as-Eins

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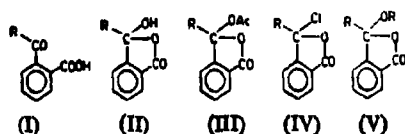
Condensation of two γ-keto acids, o-(p-methylbenzoyl)benzoic acid and o-(p-methylbenzoyl)tetrachlorobenzoic acid with phenols gives new series of phthalein dyes. These dyes are substituted phthalides in which central carbon atom is attached to two different rings and hence they have been named as phthal-as-eins, 'as' representing unsymmetry and 'ein' the class of compound (phthal-ein). Absorption maxima of these new compounds have been found comparable to those of true phthaleins.

RING-chain tautomerism is encountered in various groups of compounds, e.g., carbohydrates, alkaloides, steroides and γ-keto acids. It has been generally observed that γ-keto acids exist mainly as lactol or as a equilibrium mixture of ring (II) and chain (I) tautomers[3]. The lactol form (II) gives well crystalline acetyl derivative[3,4] (III) which still retains cyclic structure. Many reactions of γ-keto acids such as formation of pseudo chlorides (IV)[5], pseudo esters (V)[6-8] etc, have been explained on the basis of cyclization of acids to loctol IR[7,9], Raman[8] and nmr[10] spectra have further confirmed the formation of cyclic isomers.

(I) (II) (III) (IV) (V)

It has also been reported that ring tautomerism of γ-keto acids[11] is further exalted by changing R to larger alkyl or aryl groups. It increases further when hydrogen atoms on carbon atoms α to carboxyl group are also changed to larger alkyl groups or α,β-ethylenic bond[12]. In recent years Gupta *et al* reported the preparation of a large number of mixed phthaleins and succineins[18,20], by condensing various γ-keto acids with phenols. These workers proposed that γ-keto acids undergo condensation through their lactol form and hence the products possess cyclic lactonic structures. In continuation of this work, the present paper describes the synthesis of some new phthal-as-eins by condensing o-(p-methylbenzoyl)benzoic acid and o-(p-methylbenzoyl)tetrachlorobenzoic acid with various phenols.

Experimental

All melting points are uncorrected. The absorption maxima (visible) have been measured using Beckman model DU spectrophotometer in absolute ethanol (neutral and alkaline media). IR spectra were taken in KBr with a Perkin Elmer infracord. NMR spectra were recorded on Varian A-60 spectrophotometer using TMS as internal reference. For tlc, plates coated with alumina G-silica gel G (1 : 1) layers were run in ethyl acetate-methanol-5 *N* ammonia solution (60 : 30 : 10) and spots were developed with 5% aqueous NaOH.

o-(p-Methylbenzoyl)benzoic acid and o-(p-methylbenzoyl)tetrachlorobenzoic acid were prepared by reported procedure[21]. For preparation of acetyl derivative each acid was refluxed with acetic anhydride in presence of fused sodium acetate. The phenols (phenol, resorcinol, catechol, quinol, phloroglucinol and pyrogallol) were taken in slight excess of molecular proportion over the acid (VI). Conc. sulphuric acid (4-5 drops) was used as condensing agent throughout. Each dye, when tested was found free from sulphur. Analogous to phthaleins[22], the condensation is supposed to have taken place as shown in Chart 1.

(VI) (VIII) (VII) (IX) (X)

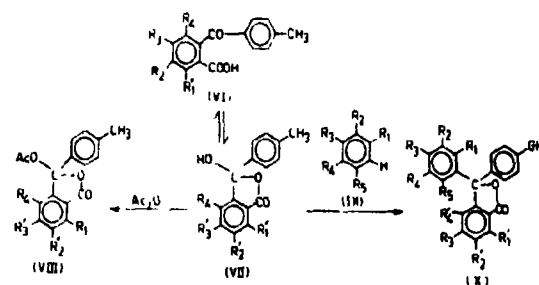



Chart 1

(VI-X) $R'_1 = R'_2 = R'_3 = R'_4 = H$ or Cl
(XI) $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = OH$
(XII) $R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OH$
(XIII) $R_3 = R_4 = R_5 = H$; $R_1 = R_2 = OH$
(XIV) $R_2 = R_3 = R_5 = H$, $R_1 = R_4 = OH$
(XV) $R_2 = R_4 = H$, $R_1 = R_3 = R_5 = OH$
(XVI) $R_4 = R_5 = H$; $R_1 = R_2 = R_3 = OH$
(XVII) $R_2 = R_4 = R_5 = H$; $R_1 = R_3 = OCOCH_3$
(XVIII) $R_5 = H$; $R_2 = R_4 = Br$; $R_1 = R_3 = OH$

Synthesis of p*-methylphenyl resorcinol tetrachlorophthal-as-ein* (XII ; $R'_1 = R'_2 = R'_3 = R'_4 = Cl$) : An intimate mixture of acid (VI ; $R'_1 = R'_2 = R'_3 = R'_4 = Cl$)

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TABLE 1—PREPARATION AND PROPERTIES OF PHTHAL-AS-EINS (X ; $R'_1 = R'_2 = R'_3 = R'_4 = H$) AND TETRACHLOROPHTHAL-AS-EINS (X ; $R'_1 = R'_2 = R'_3 = R'_4 = Cl$), RESPECTIVELY

Name of dye, (P = phthal-as-ein)	Condensation		Appearance microcrystalline. Colour	m. p. °C	Yield %	Analysis % Found (Calcd.)		
	Temp °C	Duration hr				C	H	Cl
XI (*) methylphenyl phenol P	150-160	8	yellowish white	165-166	84	79.96 (79.74)	5.28 (5.06)	
XII *p*-methylphenyl resorcinol P	130-140	3	yellowish brown	200-201	67	75.62 (75.90)	4.75 (4.93)	
XIII *p*-methylphenyl catechol P	125-130	2½	grey	172-173	61	75.71 (75.90)	5.20 (4.93)	
XIV *p*-methylphenyl quinol P	150-160	2½	brownish black	184-185	47	76.30 (75.90)	5.15 (4.93)	
XV *p*-methylphenyl phloroglucinol P	150-160	1½	brick red	212-213	60	72.69 (72.41)	4.81 (4.59)	
XVI *p*-methylphenyl pyrogallol P	130-140	1	dirty yellow	220-221	51	72.68 (72.41)	4.80 (4.59)	
XVII *p*-methylphenyl diacetylresorcinol P	130-140	3	colourless	115-116	52	77.26 (76.92)	5.01 (4.80)	
XVIII *p*-methylphenyl dibromoresorcinol P	130-140	1	brownish red	208-209	54	Br, 32.90 Br, (32.65)		
XI (*) *p*-methylphenyl phenol tetrachloro P	180-190	6	light brown	229-230	47	55.75 (55.50)	2.31 (2.64)	31.01 (31.27)
XIII *p*-methylphenyl catechol tetrachloro P	210-220	1	grey	180-181	33	53.42 (53.61)	2.79 (2.55)	30.60 (30.21)
XIV *p*-methylpheyl quinol tetrachloro P	200-210	1	brown	160-161	33	53.40 (53.61)	2.81 (2 55)	30.52 (30.21)
XV *p*-methylphenyl phloroglucinol tetrachloro P	210-220	2	red brown	245-246	50	52.00 (51.85)	2.23 (2.46)	29.05 (29.21)
XVI *p*-methylphenyl pyrogallol tetrachloro P	210-220	½	blackish brown	240-241	51	51.64 (51.85)	2.30 (2.46)	29.56 (29.21)
XVII *p*-methylphenyl diacetylresorcinoltetrachloro P	130-140	4	yellowish white	140-141	68	54.45 (54.15)	2.59 (2 88)	25.42 (25.63)
XVIII *p*-methylphenyl dibromo resorcinol tetrachloro P	room temp	over night	brick red	260-261	69		Br, 25.86 Br, (25 47)	

(*) Excess phenol after condensation was removed by steam distillation.

(7.5 g) and resorcinol (2.0 g) was taken in a hard glass boiling tube and heated in an oil bath to 180°. Conc. sulphuric acid (5 drops) was added to the homogeneous contents and heating was continued between 180-190° for 1 hr to get a hard and brittle mass on cooling. The condensed mass was crushed, washed thoroughly with water to remove excess of resorcinol and extracted with 2% aqueous NaOH. The dye was precipitated from the red pink (green fluorescent) filtrate by adding hydrochloric acid gradually with stirring. The dye was filtered, washed with water and purified by repeated crystallization from rectified spirit, dried in an oven at 110° and finally over P_2O_5 in a vacuum desiccator (yield 6.2 g ; 60%).

The dye is yellow microcrystalline solid, m.p. 250-251°. The ethanolic solution is yellow with light green fluorescence which on addition of alkali changes to red-pink with intense green fluoroscence. Found : C, 53.80 ; H, 2.67 ; Cl, 30.53 ; Mol. wt. 458 (Rast). Calcd. for $C_{21}H_{12}O_4Cl_4$; C, 53.61 ; H, 2.55 ; Cl, 30.21% ; Mol. wt. 470.

Paper chromatography of dyes (*XI*) *:* On Whatman No. 1 test paper, *n*-butanol-ammonia was allowed to run for 13 hr (descending) to give two pink spots of the dye (XI) and reference dye phenolphthalein. R_f : dye XI ($R'_1 = R'_2 = R'_3 = R'_4 = Cl$), 0.89 ; phenolphthalein, 0.91 (lit[11] R_f 0.92).

Acetylation of dyes (*XII*) *:* The dye (XII ; $R'_1 = R'_2 = R'_3 = R'_4 = Cl$) (1.0 g) was refluxed with acetic anhydride (15.0 ml) and fused sodium acetate (3.0 g) at 130-140° for 4 hr to give yellowish white acetyl derivative (0.80 g), m p. 140-141° (from acetic acid). Found : C, 54.45 ; H, 2.59 ; Cl, 25.42 ; Acetyl, 15.41. Calcd. for $C_{25}H_{16}O_6Cl_4$ or $C_{21}H_{10}O_4Cl_4(COCH_3)_2$; C, 54.15 ; H, 2 88 ; Cl, 25.63 ; Acetyl, 15.16%.

Bromination of dyes (*XII*) *:* The dye (XII, $R'_1 = R'_2 = R'_3 = R'_4 = Cl$) (1.0 g) was dissolved in absolute ethanol and bromine (2 ml) was added to it drop by drop with shaking. The contents were left overnight at room temperature. The dibromo compound separated as brick red solid (0.9 g), m.p. 260° (from 80% ethanol). It dissolves in ethanol with pinkish red colour which is intensified on addition of alkali. Found : Br, 25.86. Calcd. for $C_{21}H_{10}O_4Cl_4Br_2$; Br, 25.47%.

Caustic potash treatment of dyes (*XII*) *:* The dye (XII : $R'_1 = R'_2 = R'_3 = R'_4 = Cl$) (1.0 g) was mixed with a paste of caustic potash pellets (10.0 g) in a platinum crucible and heated at about 250° for 3 hr until the pink colour of the dye completely disappeared. The contents were cooled and dissolved in water (50 ml) and filtered. The excess of alkali was just neutralized by dil. HCl when a yellowish brown residue (A) settled down. The residue was filtered

TABLE 2—ABSORPTION MAXIMA OF PHTHAL-AS-EINS (X ; $R'_1 = R'_2 = R'_3 = R'_4 = H$) AND TETRACHLOROPHTHAL-AS-EINS (X ; $R'_1 = R'_2 = R'_3 = R'_4 = Cl$), RESPECTIVELY. G. F. = GREEN FLUORESCENCE

Dye	Colour in ethanol		Colour with 2% NaOH	λ_{max} (nm)		
	Neutral	Alkaline		Neutral	at	pH
XI	light yellow	light red	light red	500	530	9.0
XII	yellowish red (G. F.)	red	red	480	500	9.5
XIII	colourless	red	red	–	510	8.5
XIV	yellowish brown	brown	reddish brown	–	–	–
XV	yellow orange	red	red	420	460	9.0
XVI	yellow	brownish red	brownish red	–	–	–
XVII	light yellow	light yellow	light yellow	–	–	–
XVIII	light red	red	red	520	530	10.00
XI	light yellow	pink	pink	500	530	9.5
XII	yellow (light G. F.)	red pink (G.F.)	red pink (G. F.)	490	510	10.00
XIII	yellow	yellow brown	dark yellow brown	–	–	–
XIV	light yellow	light pink	light pink	–	520	9.00
XV	orange	brownish red	brownish red	450	–	–
XVI	yellow brown	green	dark green	–	–	–
XVII	light yellow	light yellow	colourless	–	–	–
XVIII	pinkish red	pinkish red	deep pink	520	530	10.00

TABLE 3—ABSORPTION MAXIMA OF SOME KNOWN PHTHALIEINS

Name of dye	Colour in ethanol		Colour with 2% NaOH	λ_{max} (nm)		
	Neutral	Alkaline		Neutral	at	pH
Phenolphthalein	colourless	pink	pink	–	550	10.5
Fluorescein	yellow red	red (G. F.)	reddish pink (G F.)	480	500	10.00
Eosin	light pink (G. F)	orange pink (G F.)	orange pink (G. F.)	530	530	9.5

and washed with water. The filtrate was further acidified by adding an excess of dil. HCl giving a white residue (B) which was also filtered and washed with water. The filtrate was extracted with ether and on evaporation of excess of solvent a brownish red residue (C) was obtained. Residues A, B and C, were identified as unreacted residual dye (XII), acid (VI) and resorcinol (XIX), respectively by direct comparision (m.m.p, co-tlc, co-ir) with their authentic samples.

Results and Discussion

o-(*p*-Methylbenzoyl)benzoic acid (VI : $R'_1 = R'_2 = R'_3 = R'_4 = H$) and *o*-(*p*-methylbenzoyl)tetrachlorobenzoic acid (VI : $R'_1 = R'_2 = R'_3 = R'_4 = Cl$) have been found spectroscopically to exist as a mixture of ring and chain tautomers. IR spectra of the acids showed notable absorption bands at 1695-1690, 1670-1660, and 1760 (very feeble) cm^{-1} indicating the presence of carboxyl >C=O, diaryl ketonic >C=O and lactonic >C=O, respectively. Broad bands at 2700-2640 and 3460-3440 cm^{-1} have been assigned to -OH of carboxyl and -OH of lactol form of the acids, respectively. The nmr spectra (DMSO-d_6) of these two acids showed the presence of a hydroxy proton of the lactol form (a broad singlet of low intensity at τ 4.7 and 4.5).

IR spectra of the acetyl derivatives of the acids showed a peak at 1780 cm^{-1} due to lactonic >C=O. Other peaks at about 1755, 1235, 1200 and 1000 cm^{-1} have been ascribed to $OCOCH_3$ group. Peaks present in the ir spectra of acids at 3460-3440, 2700-2640, 1695-1690, 1670-1660 cm^{-1} were found absent in the ir spectra of the corresponding acetyl derivatives. NMR spectra of acetyl derivatives did not contain any signal at τ 4.7 and 4.5 (present in the nmr spectra of the acids), but there was a new signal at τ 7.5 (singlet, 3H) due to $OCOCH_3$ group.

These spectral studies revealed that the acids are mixture of keto (VI) and lactol (VII) form and formation of acetyl derivatives takes place through the lactol form. Similarly, condensation of acids with phenols also occurs through the lactol form, and with excess of phenols the entire acid taken reacts as
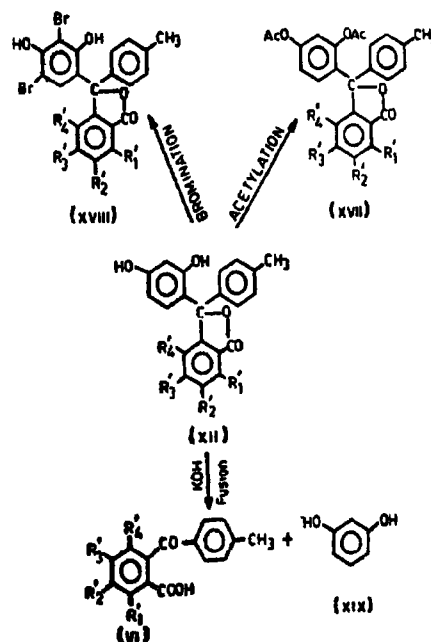
Chart 2
($R'_1 = R'_2 = R'_3 = R'_4 = H = Cl$)

lactol (VII) (Chart 1). The purity of the dyes has been confirmed by tlc and paper chromatography. The structures have been confirmed on the basis of elemental analysis, bromination, acetylation and KOH degradation studies (Chart 2). Formation of diacetyl derivatives (XVII) and dibromo derivatives (XVIII) support the presence of only one resorcinol molecule in the dyes (XII). KOH fusion of dyes (X I) yielded acids (VI) and resorcinol (XIX).

The absorption maxima of these phthal-as-eins are given in Table 2 and are comparable to those of known phthaleins prepared in similar manner (Table 3).

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Synthesis of Some New Derivatives of Azlactone (Part I)

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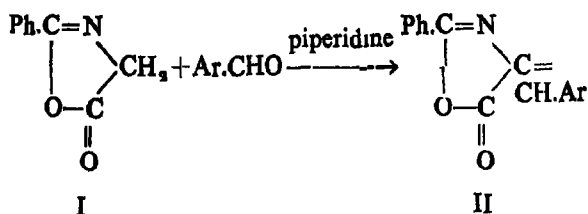
Hippuric acid azlactone (I) was condensed with aldehydes to give the corresponding arylidine azlactones (II). Compounds (II) were reacted with hydrazine hydrate, phenylhydrazine and hydroxylamine to give the corresponding pyrazolines, phenylpyrazolines and isoxazolines, respectively.

IN view of bacteriostatic[1,2] and fungicidal activities of azlactone, we undertook the synthesis of a heterocyclic system containing an azlactone ring condensed with pyrazoline, N-phenyl pyrazoline, and isoxazolines hoping that these compounds might exhibit enhanced bacteriostatic activity. The hippuric acid azlactone (I) was condensed with aldehydes in presence of piperidine as a basic catalyst to give the corresponding arylidino azlactone (II).

$$\text{Ph.C=N–CH}_2\text{–C(=O)–O (I)} + \text{Ar.CHO} \xrightarrow{\text{piperidine}} \text{Ph.C=N–C(=CH.Ar)–C(=O)–O (II)}$$

I II

The structure of compounds (II) was confirmed by elemental analysis and ir spectra, which showed a carbonyl stretching frequency at 1802 cm^{-1}, characteristic for five-membered rings[3] and a band at 1640 cm^{-1} for C=C[4].

The additive property of the exocyclic C=C in compounds (II) conjugated with the carbonyl group prompted us to investigate their behaviour towards the action of hydrazine hydrate, phenyl hydrazine and hydroxylamine hydrochloride. Interaction of II with hydrazine hydrate under suitable condition gave a variety of pyrazolines. Hydrazine hydrate interacted with II in dioxan giving unstable pyrazolines but when these were treated with glacial acetic or when the reaction was carried out in presence of glacial acetic acid, the stable N-monoacetyl pyrazoline (III) was obtained.

The structure of compounds (III) has been established by elemental analysis and ir spectra which showed absorption bands at 1687-1613 cm^{-1} (C=N) and at 1250-1227 cm^{-1} (C–N) and the absence of the -NH stretching frequency.

Phenylhydrazine reacted with II in presence of a basic catalyst. The reaction was carried out in dioxan in presence of piperridine giving N-phenyl pyrazolines (IV).

The structure of compounds (IV) was established by elemental analysis and ir spectra which showed absorption bands at 1608-1592 cm^{-1} (C=N) and at 1242-1220 cm^{-1} (C-N). Compound (IV) proved to be stable on boiling with a mixture of acetic acid and conc. sulphuric acid at room temperature or on heating above its melting point which is the condition that causes the cyclization of phenylhydrazines to pyrazolines. The prepared pyrazoline gave a colour test characteristic for aryl pyrazolines[5,6].

The isoxazoline (V) was obtained when a mixture of compound (II) and hydroxylamine in dioxan was refluxed in presence of NaOH. The structure of compounds (V) was established by elemental analysis and ir spectra which showed an absorption band at 1688-1612 cm^{-1} (C=N).

The prepared compounds (III), (IV) and (V) were tested against two bacteria, *B. subtilis* and *E. coli*, and a fungus *Aspergillus*. It was found that the compounds were more active than the parent compound (II).

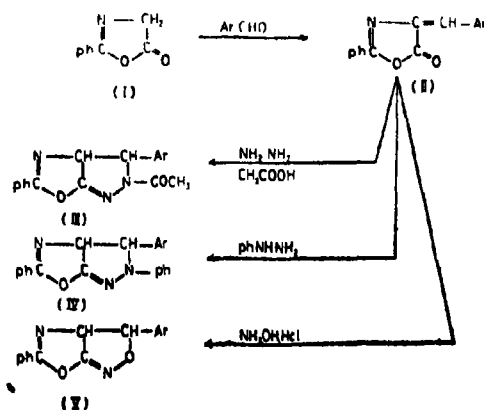



Fig. 1.

Experimental

Infra red spectra were determined in KBr pellets on an Unicam Sp. 2006 Infrared spectrophotometer. Melting points are uncorrected. Hippuric acid and hippuric acid azlactone[9] were prepared by known methods.

TABLE 1—ARYLIDINE AZLACTONE (II)

Ar	Yield %	m. p. °C	M. F.	Analysis % Found (Calcd.) C	H	N
C_6H_5	70	120-3	$C_{16}H_{11}O_2N$	76.91 (77.10)	4.11 (4.42)	5.70 (5.62)
p-OHC_6H_4	73	127-9	$C_{16}H_{11}O_3N$	72.15 (72 45)	4.18 (4.15)	5.14 (5.28)
p-$NO_2C_6H_4$	75	132-5	$C_{16}H_{10}O_4N_2$	64.91 (65.31)	3.44 (3.40)	9.74 (9.52)
o-OHC_6H_4	71	137-9	$C_{16}H_{11}O_3N$	72 05) (72 45)	4 20 (4.15)	5.20 (5.23)

TABLE 2—N-ACETYL PYRAZOLINE (III)

Ar	Yield %	m. p. °C	M. F.	Analysis % Found (Calcd.) C	H	N
C_6H_5	50	160-3	$C_{18}H_{15}O_2N_3$	70 75 (70 82)	4.89 (4.92)	13.70 (13.77)
p-OHC_6H_4	55	158-9	$C_{18}H_{15}O_3N_3$	67.00 (67 29)	4.70 (4.67)	12.95 (13.08)
p-$NO_2C_6H_4$	60	164-6	$C_{18}H_{14}O_4N_4$	61.69 (61 71)	4.05 (4.00)	16.02 (16.00)
o-OHC_6H_4	60	168-9	$C_{18}H_{15}O_3N_3$	67 20 (67.29)	4.69 (4 67)	13.12 (13.08)

TABLE 3—PHENYL PYRAZOLINE (IV)

Ar	Yield %	m. p. °C	M. F.	Analysis % Found (Calcd.) C	H	N
C_6H_5	59	140-4	$C_{22}H_{17}ON_3$	77.80 (77 88)	5 05 (5 01)	12 29 (12.39)
p-OHC_6H_4	62	158-9	$C_{22}H_{17}O_2N_3$	74 27 (74.37)	4 75 (4 79)	11.90 (11.83)
p-$NO_2C_6H_4$	63	141-2	$C_{22}H_{16}O_3N_4$	68.70 (68 75)	4.20 (4.17)	14.56 (14.58)
o-OHC_6H_4	60	160-2	$C_{22}H_{17}O_2N_3$	74 31 (74.37)	4 80 (4.79)	11.80 (11.83)

TABLE 4—ISOXAZOLINE (V)

Ar	Yield %	m. p. °C	M. F.	Analysis % Found (Calcd.) C	H	N
C_6H_5	65	170-3	$C_{16}H_{12}O_2N_2$	72.63 (72.73)	4.60 (4.55)	10.65 (10.61)
p-OHC_6H_4	60	167-3	$C_{16}H_{12}O_3N_2$	68 51 (68 57)	4 30 (4 29)	10.01 (10.00)
p-$NO_2C_6H_4$	63	175-7	$C_{16}H_{11}O_4N_3$	60.20 (60.19)	3.50 (3.45)	13.20 (13 17)
o-OHC_6H_4	60	180-1	$C_{16}H_{12}O_3N_2$	68 49 (68 57)	4.25 (4.29)	10.01 (10.00)

TABLE 5—ANTIMICROBAL ACTIVITY

Comp.	*B. subtilis*	*E. Coli*	*Aspergillus*
II	+	+	+ve
III	+++	++	+ve
IV	++	++	+ve
V	+++++	++++++	+ve

Arylidine azlactone (II) : Equimolar amounts (0.1 mole) of hippuric acid azlactone and aromatic aldehyde were refluxed in dioxan (25 ml) containing piperidine (1 ml) for 1 to 3 hr. The reaction mixture was allowed to cool and arylidine azlactone was precipitated with petroleum ether (80-100). The product was filtered off, washed several times with petroleum ether and crystallized from ethanol. The results are given in Table 1.

N-Acetyl pyrazoline (III) : A mixture of arylidine azlactone (II) (0.1 mole) hydrazine hydrate (0.1 mole) and a few drops of glacial acetic acid in dioxan (25 ml) was heated under reflux for 3 hr. The reaction mixture concentrated when the N-acetyl pyrazoline separated. It was filtered and recrystallized from benzene. The results are listed in Table 2.

N-Phenyl pyrazoline (IV) : Equimolar amounts of arylidine azlactone (II) and phenyl hydrazine were refluxed in dioxan (30 ml) containing a few drops of piperidine for 3 hr. The reaction mixture was allowed to cool and the N-phenyl pyrazoline was precipitated with petroleum ether. The product was filtered washed several times with petroleum ether (80-100) and crystallized from the same solvent. The results are listed in Table 3.

Isoxazoline (V) : A mixture of arylidine azlactone (II) (0.1 mole), hydroxylamine hydrochloride (0.1 mole) and a few pellets of NaOH in dioxan (30 ml) was heated under reflux for 3 hr. The reaction mixture was filtered and the precipitate washed thoroughly with dioxan. The isoxazoline was precipitated from the filtrate by ether. The product was filtered, washed several times with ether and recrystallized from the benzene. The results are listed in Table 4.

Biological testing : The bacteria used for testing were *B. subtilis* (gram positive) and *E. coli* (gram negative). The fungus used for testing was *Aspergillus*. The data are listed in Table 5.

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Synthesis of Pericarbonyl Lignans and Their Analogues

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Perkin condensation of β-benzoylpropionic acid system (VI) and aryl aldehyde gave butenolide (VII) which led to α-arylidene-β-benzoylpropionic acid (IX). The latter, on formylation followed by cyclization afforded chloromethylnaphthoic acid (XV). Chloromethyl derivatives (XV) were subsequently converted into pericarbonyl lactones (XVI). This approach exemplifies a simple synthetic route to 1-aryl-2,3-naphthalide pericarbonyl lignans.

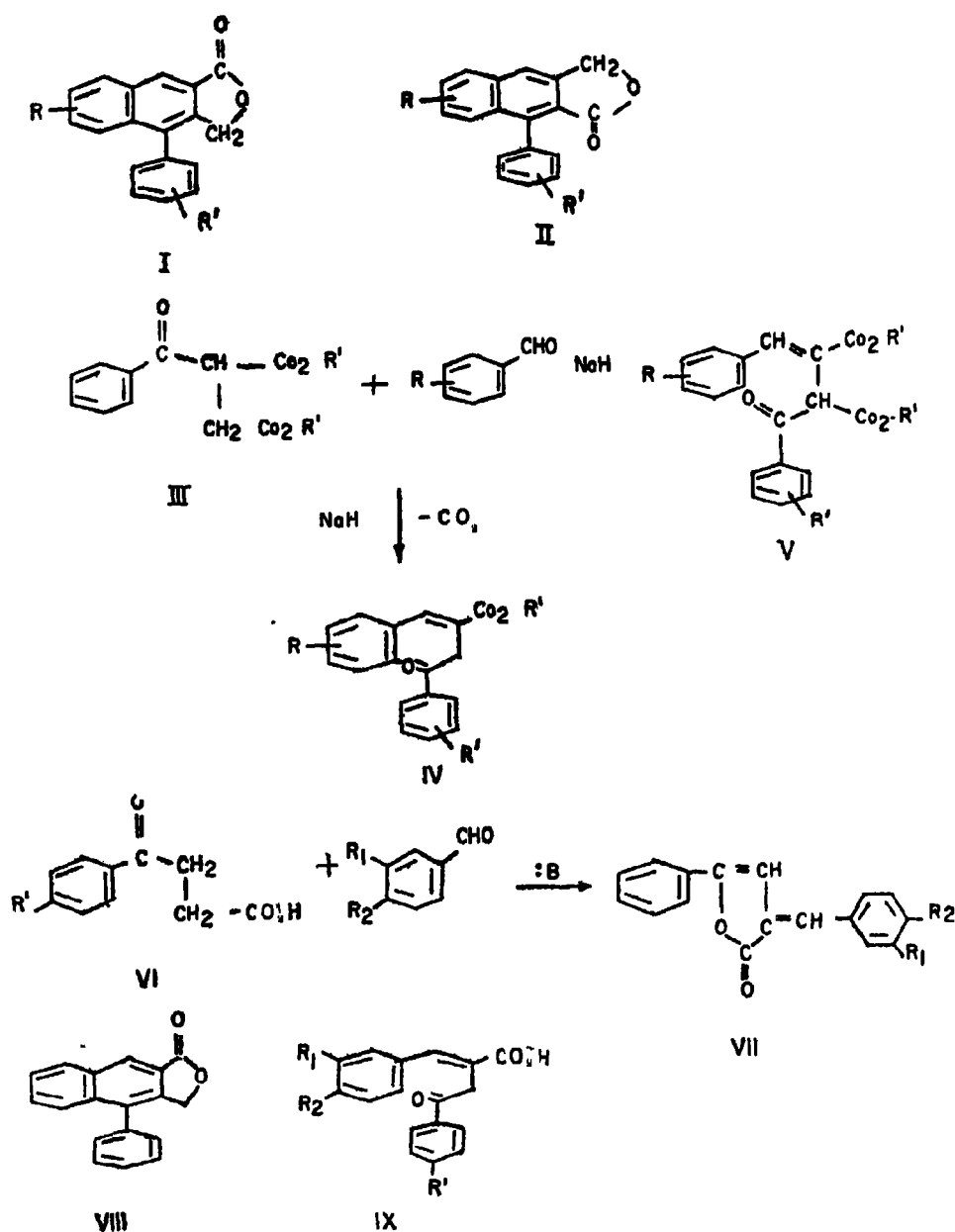
NATURAL products based on 2,3-dimethylphenylnaphthalene constitute a distinct class of lignans. More than 10 members, dehydropodophyllotoxin[1a], diphyllin[1b-1g], justicidin D[1h] (neojusticidin[1i]), justicidin E[1j,k], taiwanin A[1l], taiwanin C[1m] and helioxanthin[1n], are now well characterized. All are lactones of either 1-phenyl-2-hydroxymethylnaphthalene-3-carboxylic acid (pericarbonyl lactone) (I) or 1-phenyl-3-hydroxymethylnaphthalene-2-carboxylic acid (perimethylene lactone) (II). Some of the arylnaphthalide lignans were found to be physiologically active. Prominent among them are diphyllin[2] and justicidins A and B which are fish poisons, the latter being comparable to rotenone in toxicity in *Orizius latipus*[3]. Diphyllin completely inhibited DNA synthesis in Ehrlich carcinoma cells within a minute and partially inhibited RNA and protein formation[4]. The synthesis of some arylnaphthalide lignans with pericarbonyl grouping is reported here.

An earlier attempt[5] to prepare the system of the type (I) by condensation of dimethylbenzoylsuccinate (III) and aryl aldehyde proceeded with the loss of carbomethoxy group leading to α-arylidene-β-benzoylpropionate (IV) which was later converted into pericarbonyl system (I).

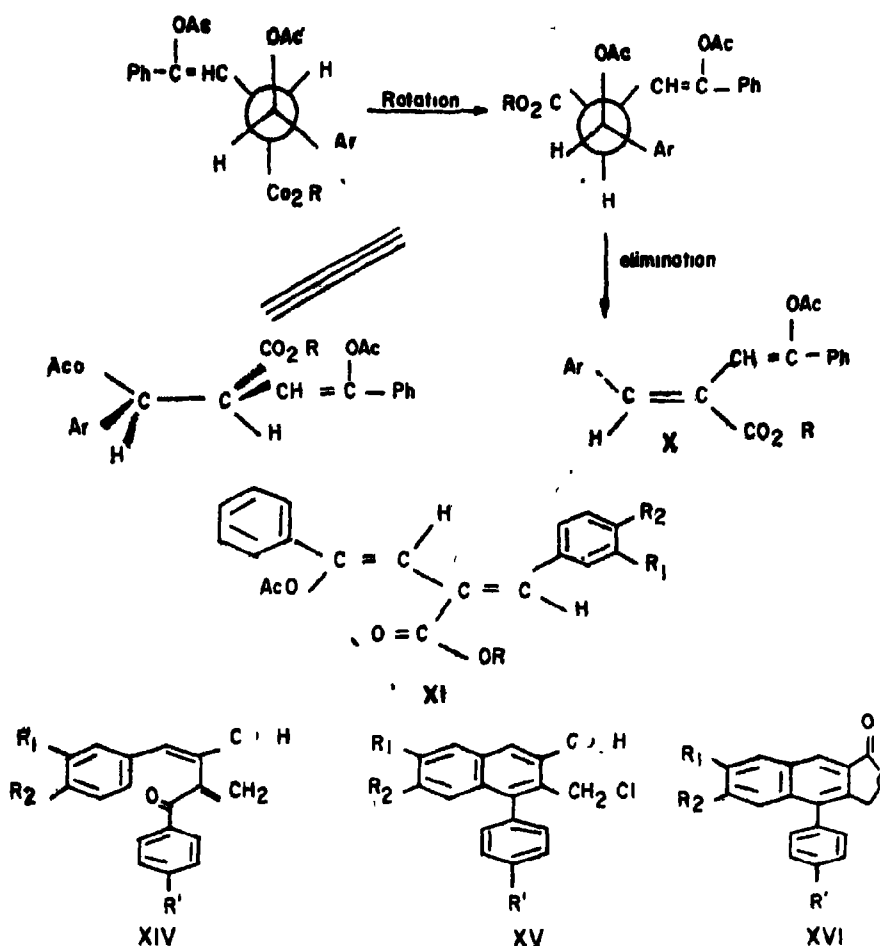
To prepare pericarbonyl lactone (I) it was endeavoured to use β-aroylpropionic acid system (VI) which has two reactive methylene groups and a carboxy function capable of being handled to lead to the basic skeleton of lignan (VIII). A carbomethoxy group would yield part of furan ring adjacent to ring B and oxo group could be reduced.

Perkin condensation of β-benzoylpropionic acid (VI) with aryl aldehyde yielded butenolide of the type (VII) which finally led to α-arylidene-β-benzoylpropionic acid (IX). The butenolides (VII) were highly insoluble in most solvents, non-acidic to bicarbonate, but slowly dissolved in sodium hydroxide. Equivalent weight determination was not satisfactory (the products were highly insoluble and slight decomposition occurred). Using substituted benzoylpropionic acids and different aryl aldehydes, a number of butenolides were synthesized. These compounds showed an extended conjugation at 400 nm in their ultraviolet spectra[6]. IR spectra of these compounds showed characteristic absorption at 1775 to 1760 cm^{-1} (lactone carbonyl[7]) and nmr showed all protons in the expected region 6.58 to 7.58δ (Table 1).

When the butenolide corresponding to benzaldehyde (VII ; $R_1=R_2=R'=H$) was treated with 30% sodium hydroxide with subsequent acidification, the products isolated were benzaldehyde and benzoic acid, respectively. A retro reaction occurred[8]. The butenolides (VII) were hence cleaved by refluxing in methanolic sodium carbonate (Borsche[9]), on acidification, afforded dark coloured mass which crystallized from aqueous alcohol to give α-arylidene-β-benzoylpropionic acids (IX). The ir spectra of IX showed a single absorption at 1681 cm^{-1} (aryl conjugated carbonyl and α,β-unsaturated acid[10,11]) (Table 2).

The stereochemistry of formation of α-arylidene-β-benzoylpropionic acids by Perkin condensation of β-benzoylpropionic acids with aryl aldehyde has E or *cis* Ar/CH_2COPh structure (X)[8]. The stereochemistry of the product would be controlled by the transition state in the Perkin reaction having the conformation with the bulky Ar and COOR groups *trans* which undergoes *trans* elimination of acetic acid to give the product (XI)[10,11], with *cis* (E) Ar/CH_2COPh stereochemistry. Zimmerman orbital overlap theory[12] also leads to the same stereochemistry. For the overlap control, the carbonyl group must lie in the plane of the incipient double bond between the carbon 2 and 3. Out of the two transition states, (XII) and (XIII), which are possible in Perkin reaction (XII) would lead to *cis* (E) Ar/CH_2COPh. In the transition state (XII), the planarity which is necessary for orbital overlap is readily achieved as carbonyl group is unhindered. But in the case of (XIII), there is steric interaction of *cis* aryl/carbonyl groups which pushes the carbonyl group out of plane of the incipient double bond(XIIIa). So, the planarity is less readily achieved and consequently the overlap control is less. Thus the transition state (XII) is more favourable.

Scheme 1

α-Arylidene-β-benzoylpropionic acid system (IX) thus obtained contained the required skeleton to prepare pericarbonyl lactone system. Elements of furan ring adjacent to ring B were introduced by formylation. Acid (IX) was treated with aqueous formaldehyde and potassium hydroxide to give the product which was identified as α-arylidene-β-methylene-β-benzoylpropionic acid (XIV). [Kulkarni[13,14] observed that alkali concentration in the reaction play an important role in the formation of either mono or dicondensation product]. IR spectra of XIV showed a broad peak at 1660 cm^{-1} for carboxyl and keto groups. In the nmr spectrum, two methylene protons appeared as a singlet at 6.06δ, and a singlet at 7.85δ was assigned for olefinic proton (Table 3).

To cyclize the α-arylidene-β-methylene-β-benzoylpropionic acid system (XIV) to 1-phenyl-naphthalene system, it was treated with a mixture of acetic acid and conc. hydrochloric acid to give a product which was characterized as 1-phenyl-2-chloromethyl-naphthalene-3-carboxylic acid (XV). IR spectra of chloromethyl derivatives (XV) showed a peak at 1670 cm^{-1} for a carboxyl group. NMR spectra showed a singlet at 5.08δ for chloromethyl protons. The proton at C_8 appeared as a singlet at 6.68δ. The proton at C_4 showed a singlet at 8.74δ. A

Scheme 2

glet due to C_8 proton at 7.35δ is merged in ›matic pattern in the region 7.3-7.78δ (Table 4).

Chloromethyl derivatives (XV) were hydrolysed heating with 10% aqueous sodium hydroxide. ›n they were treated with excess of hydrochloric i and heated at 100° for 0.5 hr. After cooling, solid was isolated and identified as 1-phenyl-2-lroxymethylnaphthalene-3-carboxylic acid lactone /I). In ir spectra of XVI, absorption at 1760 · indicated the presence of 5-membered lactone ;[16]. The nmr spectra are also consistent with structures assigned to them. 4-H proton reso-›s close to 8.38δ (compared to 7.7δ in retro one[16]) whilst methylene group of lactone[17] is ›lded by ring current. This is seen by the mical shift near 5.10δ in contrast to 5.40δ in retro lactone (Table 5).

›erimental

All melting points are uncorrected. The ir ›tra were run on Perkin-Elmer 237 grating ›hine in nujol and uv on Beckmann DB-4 spec-›hotometer in ethanol unless otherwise stated. ·R spectra were measured at 60 MHz using ›terochloroform ($CDCl_3$) as the solvent, the chemical shifts are given in ppm using tetramethylsilane (TMS) as an internal standard.

1. *Perkin condensation of β-benzoylpropionic acid and veratraldehyde ; α - (3,4-Dimethoxybenzylidene) - γ - phenyl- Δ β,γ-butenolide* (VIIa, $R_1=R_2=OCH_3$, $R'=H$) :

Veratraldehyde (4.2 g ; 0.025 m) and β-benzoylpropionic acid (4.9 g ; 0.025m) were refluxed for 3 hr in presence of acetic anhydride (7.5 ml) and a drop of pyridine. The hot reaction mixture was added to cold water (100 ml) and was warmed for a minute, cooled to 0°, filtered, washed with water, dried and crystallized from benzene to give α-(3,4-dimethoxybenzylidene) -γ-phenyl - Δβ,γ - butenolide (VIIa), m.p, 125° UV : λ_{max}^{EtOH} 249 nm, log ε 4.21, 3.91 nm, log ε 4.21 an shoulder 406 nm, log ε 4.24. (Found : C, 73.56 ; H, 5.96. Calcd. for $C_{19}H_{16}O_4$; C, 74.02 ; H, 5.23%. Table 1 presents the data for other butenolides (VIIa-VIIr).

2. *α-(3,4-Dimethoxybenzylidene)-β-benzoylpropionic acid* (IXa, $R_1=R_2=OCH_3$, $R'=H$) :

α-(3,4-Dimethoxybenzylidene)-γ-phenyl-Δβ,γ-butenolide (VIIa) (5 g) was refluxed with alcoholic sodium carbonate solution for 5 hr. The resulting mixture was cooled, filtered and acidified to congo

TABLE 1—α-ARYLIDENE-γ-PHENYL-Δβ,γ-BUTENOLIDES (VII)

Condensation of β-Aroylpropionic Acid with Aldehydes

Sl. No.	Aldehyde g	β-Aroylpropionic acid g	Lactone g	Yield %	m.p. °C	UV λ_{max}^{EtOH} nm (log ε)	IR cm⁻¹	NMR δ	Analysis % Found C	Found H	Calcd. C	Calcd. H
1.	Veratraldehyde 8.3	β-Benzoylpropionic acid 8.9	(VIIa) 14 1	73.3	125	249 (4.21) 392 (4.32) 406 (4.24)	– –	–	73.56	5.96	74.02	5.23
2	Veratraldehyde 8 3	4-Methoxybenzoylpropionic acid 10 4	(VIIb) 14 6	82 8	172	–	–	–	70.59	5.17	71.00	5.36
3.	Veratraldehyde 8.3	4-Methylbenzoylpropionic acid 9.6	(VIIc) 12 1	75.1	170	–	–	–	74.14	5.28	74.53	5.63
4.	Vanillin 7.1	β-Benzoylpropionic acid 8.9	(VIId) 13.7	85 6	147	252 (4.18) 393 (4.26)	–	–	–	–	–	–
5.	Vanillin 7.1	4-Methoxybenzoylpropionic acid 10.4	(VIIe) 11.7	72.2	188	–	–	–	70.12	4.58	70.37	4.97
6.	Vanillin 7.1	4-Methylbenzoylpropionic acid 9.6	(VIIf) 13.1	85 0	156	–	–	–	74.22	4.95	74.01	5.23
7.	Vanillin 7.1	4-Isopropylbenzoylpropionic acid 11.0	(VIIg)	77 0	122	–	–	–	74.79	6.03	74.97	5.99
8.	Vanillin 7.1	4-Chlorobenzoylpropionic acid 10.6	(VIIh) 11.5	70 0	–	–	–	–	–	–	–	–
9.	Vanillin 7.1	4-Bromobenzoylpropionic acid	(VIIi)	63.2	128	–	–	–	–	–	–	–
10.	4-Methoxybenzaldehyde 6 8	β-Benzoylpropionic acid 8 9	(VIIj) 13.2	84.1	169	245 (4.28) 290 (4.20) 402 (4.23)	1772 1762	3.87 (s, 3H, OCH_3) 7.11-7.06 (m, 9H aromatic), 6.92 (s, 2H, olefinic)	77.66	5.07	77.69	5.07
11.	3-Methoxybenzaldehyde 6 8	β-Benzoylpropionic acid	(VIIk)	81.3	120	–	–	–	77.18	5.27	77 69	5.07
12.	3-Methoxybenzaldehyde 6 8	4-Methoxybenzoylpropionic acid 10 4	(VIIl) 11 0	71.4	135	–	–	–	–	–	–	–
13.	Piperonal 7.5	β-Benzoylpropionic acid 8 9	(VIIm) 14.0	85.4	166	254 (4.12) 404 (4.46)	1772 1862	6.03 (s, 2H, $-OCH_2O-$) 7.85-6.91 (m, 8H aromatic), 6.78 (s, 2H, olefinic)	73.48	4.59	73 97	4.14
14.	Piperonal 7.5	4-Methoxybenzoylpropionic acid 10.4	(VIIn) 12.1	76.1	115	–	–	–	71.65	4.54	70.80	4.38
15.	Piperonal 7.5	4-Methylbenzoylpropionic acid 9.6	(VIIo) 12.0	82.1	190	–	–	–	–	–	–	–

Contd. Table 1

(*Contd. Table 1*)

Sl. No.	Aldehyde	β-Aroyl-propionic acid	Lactone	Yield	m.p.	UV λ_{max}^{EtOH}	IR	NMR	Analysis % Found		Calcd.	
	g	g	g	%	°C	nm (log ε)	cm⁻¹	δ	C	H	C	H
16.	Piperonal 7.5	4-Ethyl-benzoyl-propionic acid 10.3	(VIIp) 10.0	65.4	137	–	–	–	74.59	4.75	74.99	5.04
17.	Piperonal 7.5	4-Isopro-pylbenzoyl-propionic acid 11.0	(VIIq) 14.3	85.1	114	–	–	–	75.25	5.67	75.44	5.43
18.	Piperonal 7.5	4-Chloro-benzoyl-propionic acid 10.6	(VIIr)	66.7	245	–	–	–	–	–	–	–

TABLE 2—α-ARYLIDENE-β-BENZOYLPROPIONIC ACID (IX)

Sl. No.	R	Eq. wt. Found	Eq. wt. Calcd.	m.p. °C	UV λ_{max}^{EtOH} nm (log ε)	IR cm⁻¹	NMR δ	Analysis% Found C	H	Calcd. C	H
1	IXa : $R_1 = R_2 = OCH_3$, $R' = H$	323	326	169	233(4.17) 274(3.99) 398(3.85)	1681	—	70.41	5.12	69.93	5.56
2.	IXb : $R_1 = R_2 = R' = OCH_3$	349	356	192	—	1681	—	67.82	5.56	67.40	5.66
3.	IXc : $R_1 = R_2 = OCH_3$, $R' = CH_3$	338	340	196	—	1682	2.43 (s, 3H, $-CH_3$) 3.63 and 3.80 (s, 6H, 2-OCH_3), 4.23 (s, 2H, $-CH_2$), 6.83-7.97 (m, 7H, aromatic and olefinic protons)	69.67	5.35	70.56	5.92
4.	IXd : $R_1 = OCH_3$, $R_2 = OH$, $R' = H$	317	312	207	233(4.39) 289(4.19)	–	–	69.63	4.92	69.23	5.16
5.	IXe : $R_1 = OCH_3$, $R_2 = OH$, $R' = OCH_3$	339	342	211	—	1682	3.68 and 3.95 (s, 6H, 2-OCH_3), 4.28 (s, 2H, $-CH_2$), 7.14 (s, 1H, -OH), 6.90-8.10 (m, 8H, olefinic and aromatic protons)	66.90	5.06	66.66	5.30
6.	IXf : $R_1 = OCH_3$, $R_2 = OH$, $R' = CH_3$	330	326	223	—	1681	–	70.41	5.25	69 93	5.56
7.	IXg : $R_1 = OCH_3$, $R_2 = OH$, $R' = CH(CH_3)_2$	348	354	163	—	1682	–	71.48	6.42	71.16	6.26
8.	IXh : $R_1 = OCH_3$, $R_2 = OH$, $R' = Cl$	341	346.5	213	—	–	–	–	–	–	–
9.	IXi : $R_1 = OCH_3$		391.0	—	—	–	–	–	–	–	–
0.	IXj : $R_1 = R' = H$, $R_2 = OCH_3$	293	296	177	245(4.28) 275(4.30) 296(4.05)	–	–	73.24	6.03	72.98	5.44
1.	IXk : $R_1 = OCH_3$, $R_2 = R' = H$	291	296	145	—	–	–	–	–	–	–
2	IXl : $R_1R_2 = -OCH_2O-$, $R' = H$	307	310	203	237(4.42)	1682	4.30 (s, 2H, $-CH_2$), 6.12 (s, 2H, $-OCH_2O-$), 6.98-8.2 (m, 9H, aromatic protons)	70.41	4.96	69.68	4.55
3	IXm : $R_1R_2 = -OCH_2O-$, $R' = OCH_3$	335	340	—	—	–	–	66.75	4.32	67.06	4.74
4.	IXn : $R_1R_2 = -OCH_2O-$, $R' = CH_3$	320	324	196	—	–	–	69.92	4.78	70.37	4.97
5.	IXo : $R_1R_2 = -OCH_2O-$, $R' = C_2H_5$	342	338	—	—	–	–			–	
6.	IXp : $R_1R_2 = -OCH_2O-$, $R' = CH(CH_3)_2$	348	352	161	—	–	–			–	
7.	IXq : $R_1R_2 = -OCH_2O-$, $R' = Cl$	337	344.5	—	—	–	–			–	
8.	IXr : $R_1 = R' = OCH_3$, $R_2 = H$		326	142	—	–	–			–	

TABLE 3—α-ARYLIDENE-β-METHYLENE-β-BENZOYLPROPIONIC ACIDS (XIV)

Sl. No.	R	Eq. wt Found	Eq. wt. Calcd.	m. p. °C	UV : λ_{max}^{EtOH} nm (log ε)	IR : cm^{-1}	NMR δ	Analysis % Found C	Found H	Calcd. C	Calcd. H
1.	XIVa : $R_1 = R_2 = OCH_3$, $R' = H$	332	338	125	235 (4.21) 282 (4.08)	1660	3.82 and 3.90 (s, 6H, -2OCH$_3$), 6.06 (s, 2H, -C=CH$_2$), 6.8-8.0 (m, 9H, aromatic and olefinic protons)	70.65	5.02	71.00	5.36
2	XIVe : $R_1 = R' = OCH_3$, $R_2 = OH$	348	354	201	–	1660	–	67.41	5.34	67.80	5.12
3.	XIVi : $R_1 = OCH_3$, $R_2 = R' = H$	302	308	170	–	–	–	73.68	5.31	74.02	5.23
4.	XIVj : $R_1 = R' = H$, $R_2 = OCH_3$	304	308	144	–	–	–	–	–	–	–
5.	XIVl : $R_1R_2 = -OCH_2O-$, $R' = H$	317	322	–	–	1650	5.99-6.02 (d, 2H -C=CH$_2$), 6.15 (s, 2H, -OCH$_2$O$^-$), 6.93-8.0 (m, 9H, aromatic and olefinic protons)	71.24	4.09	70.80	4.38

TABLE 4—1-PHENYL-2-CHLOROETHYL-NAPHTHALENE-3 CARBOXYLIC ACIDS

Sl. No.	R	Eq. wt. Found	Eq. wt. Calcd.	m. p. °C	UV λ_{max}^{EtOH} nm (log ε)	IR cm^{-1}	NMR δ	Analysis % Found C	Found H	Calcd. C	Calcd. H
1.	XVa : $R_1 = R_2 = OCH_3$, $R' = H$	351	356.8	217	235 (4.21) 282 (4.08)	1670	3.74 and 4.07 (s, 6H, 2-OCH$_3$), 5.08 (s, 2H, -CH$_2$-Cl), 6.68 (s, 1H, C$_8$-H), 7.35 (s, 1H, C$_5$-H), 7.45-7.68 (m, 5H, phenyl) and 8.74 (s, 1H, C$_4$-H)	66.96	4.73	67.33	4.80
2.	XVb : $R_1 = R_2 = R' = OCH_3$	380	386 8	179	–	1670	–	–	–	–	–
3.	XVc : $R_1 = R_2 = OCH_3$, $R' = CH_3$	366	370.8	209	–	1671	–	67.79	5.01	68.02	5 16
4.	XVd : $R_1 = OCH_3$, $R_2 = OH$, $R' = H$	335	342.8	179	–	1670	–	–	–	–	–
5.	XVe : $R_1 = R' = OCH_3$, $R_2 = OH$	366	372.8	212	–	–	–	–	–	–	–
6.	XVf : $R_1 = OCH_3$, $R_2 = OH$, $R' = CH_3$	352	356 8	–	–	–	–	–	–	–	–
7.	XVg : $R_1 = OCH_3$, $R_2 = OH$, $R' = CH(CH_3)_2$	380	384.8	196	–	1672	–	68.26	5.37	68.66	5.50
8.	XVk : $R_1 = OCH_3$, $R_2 = R' = H$	321	326.8	201	–	–	–	–	–	–	–
9.	XVl : $R_1 = R' = OCH_3$, $R_2 = H$	348	356.8	–	–	–	–	–	–	–	–
10.	XVm : $R_1R_2 = -OCH_2-$, $R' = H$	336	340.8	241	–	–	–	67.32	3.41	66.96	3.84
11.	XVn : $R_1R_2 = OCH_2O-$, $R' = CH_3$	351	354.8	245	–	1671	–	67.47	4.56	67.70	4.26
12.	XVo : $R_1R_2 = -OCH_2O-$, $R' = CH(CH_3)_2$	376	382.8	229	–	–	–	68.77	4.69	69.01	5.00

TABLE 5—1-ARYL-2-HYDROXYMETHYLNAPHTHALENE-3-CARBOXYLIC ACID LACTONES

Sl. No.	R	m.p. °C	UV : λ_{max}^{EtOH} nm (log ε)	IR cm^{-1}	NMR δ	Analysis % Found C	H	Calcd. C	H
1.	XVIa : $R_1 = R_2 = OCH_3$, $R' = H$	205	258 (4.69) 314 (4.02)	1760	3.85 and 4.06 (s, 6H, 2-OCH_3), 5.22 (s, 2H, lactone CH_2), 7.16 (s, 1H, C_8-H), 7.37 (s, 1H, C_5-H), 7.6 (br. s, 5H, phenyl) and 8.36 s, 1H, C_4-H)	75.04	5.39	74.99	5.04
2.	XVIb : $R_1 = R_2 = R' = OCH_3$	230	–	1761	3.90, 4.01, 4.25 (s, 9H, 3-OCH_3), 5.30 (s, 2H, lactone CH_2), 7.1-7.7 (m, 6H, aromatic), 8.4 (s, 1H, C_4-H)	72.37	4.86	72.00	5.18
3.	XVIc : $R_1 = R_2 = OCH_3$, $R' = CH_3$	214	–	1762	2.50 (s, 3H, -CH_3), 3.86 and 4.08 (s, 6H, 2-OCH_3), 5.23 (s, 1H, lactone CH_2), 7.16-7.40 (m, 6H, aromatic), 8.33 (s, 1H, C_4-H)	75.39	5.24	75.44	5.43
4.	XVId : $R_1 = OCH_3$, $R_2 = OH$, $R' = OCH_3$	220	–	–	–	–	–	–	–
5.	XVIe : $R_1 = OCH_3$, $R_2 = OH$, $R' = CH_3$	241	–	1760	2.47 (s, 3H, -CH_3), 3.83 (s, 3H, -1 OCH_3), 5.20 (s, 2H, lactone CH_2), 7.04-7.30 (m, 7H and 1H, -OH aromatic) 8.25 (s, 1H, C_4-H)	74.68	4.73	74.99	5.04
6.	XVIf : $R_1 = OCH_3$, $R_2 = OH$, $R' = CH(CH_3)_2$	244	–	1762	–	76.06	5.45	75.83	5.79
7.	XVIg : $R_1 = OCH_3$, $R_2 = H' = H$	172	–	–	3.97 (s, 3H, -OCH_3), 5.21 (s, 2H, lactone CH_2), 7.17–7.83 (m, 8H, aromatic), 8.33 (s, 1H, C_4-H)	78.25	4.34	78.60	4.86
8.	XVIh : $R_1R_2 = OCH_2O$–, $R' = H$	211	–	–	–	–	–	–	–
9.	XVIi : $R_1R_2 = OCH_2O$–, $R' = CH_3$	171	–	1672	2.50 (s, 3H, -CH_3), 5.23 (s, 2H, lactone CH_2), 6.10 (s, 2H, -OCH_2O-), 7.13 – 7 4 (d, 6H aromatic), 2.28 (s, 1H, C_8-H)	75.19	4.23	75.46	4.43
10.	XVIj : $R_1R_2 = -OCH_2O$–, $R' = CH(CH_3)_2$	241	–	–	–	76.73	4.87	76.29	5.24

red with HCl (3*N*). It gave a solid which was crystallized and identified as α-(3,4-dimethoxybenzylidene)-β-benzoylpropionic acid (4.6 g). Recrystallized from aqueous ethanol, m.p. 169°. Eq. wt. Found 324; Calcd. for $C_{19}H_{18}O_5$; 326. IR : ν_{CO} (nujol) 1650 cm^{-1} (α,β-unsaturated ketone and carboxylic acid). (Found : C, 70.41; H, 5.12. Calcd. for $C_{19}H_{18}O_5$; C, 69.92 H, 5.56%). Table 2 presents data for other acids (IXa-IXr).

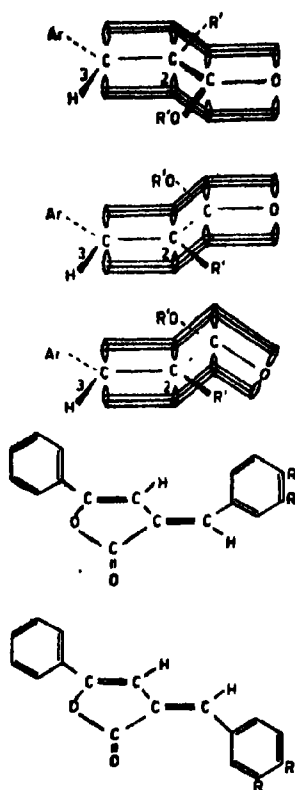
3. *α-(3,4-Dimethoxybenzylidene)-β-methylene-β-benzoylpropionic acid* (XIVa, $R_1 = R_2 = OCH_3$, $R' = H$):

To a solution of α-(3,4-dimethoxybenzylidene)-β-benzoylpropionic acid (IXa) in 10% aqueous sodium hydroxide (9 ml) was added 40% formalin solution (6 ml) and the reaction mixture was left overnight at room temperature. It was then cooled, acidified and extracted with benzene (3×50 ml) and dried ($MgSO_4$). Evaporation of the solvent led to an orange gum (2.3 g) crystallized from benzene-petroleum ether (40-60) to give a solid, m.p. 125-126°, which was identified as α-(3,4-dimethoxybenzylidene)-β-methylene-β-benzoylpropionic acid. UV : λ_{max}^{EtOH} 235 nm (log ε 4.21) and 282 nm (log ε 4.08). IR : ν_{CO} (nujol) 1660 cm^{-1} (C=O and CO_2H merged). NMR : ($CDCl_3$) δ 3.82 and 3.90 (s, 6H, 2-OCH_3), 6.06 (s, 2H, C=CH_2), 6.8-8.0 (m, 9H, aromatic and olefinic protons). Table 3 presents data for other methylenic compounds (XIVa-XIVl).

4. *1-Phenyl-2-chloromethyl-6,7-dimethoxynaphthalene-3-carboxylic acid* (XVa, $R_1 = R_2 = OCH_3$, $R' = H$):

Conc. hydrochloric acid (50 ml) was gradually added to a cold solution of α-(3,4-dimethoxybenzylidene)-β-methylene-β-benzoylpropionic acid (XIVa) (2.6 g) in glacial acetic acid (20 ml) and the mixture left overnight at room temperature. The yellow precipitate (2.2 g) formed was collected and crystallized from methanol to give a pale yellow solid, m.p. 217°, Eq. wt. Found 355; Calcd. for $C_{20}H_{17}O_4Cl$; 356.5. UV : λ_{max}^{EtOH} 252 (log ε 4.79) and 287 (log ε 3.93). IR : ν_{CO} (KBr) 1670 cm^{-1} (COOH gr). NMR : ($CDCl_3$) δ 3.74 and 4.07 (s, 6H, 2-OCH_3), 5.08 (s, 2H, -CH_2Cl), 6.68 (s, 1H, C_8-H), 7.35 (s, 1H, C_5-H), 7.45-7.68 (m, 5H, phenyl) and 8.74 (s, 1H, C_4-H). (Found : C, 66.96; H, 4.73. Calcd. for $C_{20}H_{17}O_4$-Cl; C, 67.33; H, 4.80%). Table 4 presents data for other chloromethyl derivatives (XVa-XVo).

5. *1-Phenyl-2-hydroxymethyl-6,7-dimethoxynaphthalene-3-carboxylic acid lactone* (XVIa, $R_1 = R_2 = OCH_3$, $R' = H$):

The chloromethylnaphthoic acid (XVa) (2.0 g) was dissolved in 10% sodium hydroxide (15 ml) and

Scheme 3

heated at 100° for 1 hr. The mixture was cooled and washed with water to give a yellow solid (1.7 g). Crystallization from chloroform-methanol gave light yellow prisms, m.p. 205°, of 1-phenyl-2-hydroxymethyl-6,7-dimethoxynaphthalene-3-carboxylic acid lactone (XVIa). UV : λ_{max}^{EtOH} 258 (log ϵ 4.69) and 314 nm (log ϵ 4.02). IR : ν_{CO} (KBr) 1670 cm^{-1} (lactone). NMR : $CDCl_3$ δ 3.85 and 4.06 (s, 6H, 2-OCH_3), 5.22 (s, 2H, lactone CH_2), 7.16 (s, 1H, C_8-H), 7.37 (s, 1H, C_5-H), 7.16 (br, s, 5H phenyl) and 8.36 (s, 1H, C_4-H). Table 5 presents data for other pericarbonyl lactones (XVIa-XVIj).

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Synthesis of Aryloxy/Aryl Acetyl Thiosemicarbazides, Substituted 1,3,4-Oxadiazoles, 1,3,4-Thiadiazoles, 1,2,4-Triazoles and Related Compounds as Potential Fungicides

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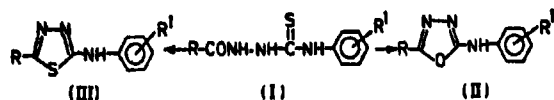
Twelve 1-aryloxy/aryl acetyl-4-aryl thiosemicarbazides, twelve 2-arylamino-5-aryloxy/aryl methyl-1,3,4-oxadiazoles, eleven 2-arylamino-5-aryloxy/aryl methyl-1,3,4-thiadiazoles, twelve 3-aryloxy/aryl methyl-4-aryl-5-mercapto-1,2,4-triazoles, three methyl-(3-aryloxymethyl-4-aryl-1,2,4-triazol-5-yl)-sulphides, three *bis*-(3-aryloxymethyl-4-aryl-1,2,4-triazol-5-yl)-disulphides and six *bis*-(3-aryloxy/aryl methyl-4-aryl-1,2,4-triazol-5-yl)-alkylene disulphides were prepared. Forty nine compounds have been screened against *A. niger* and *H. oryzae* and were found to possess moderate to fairly good antifungal activity.

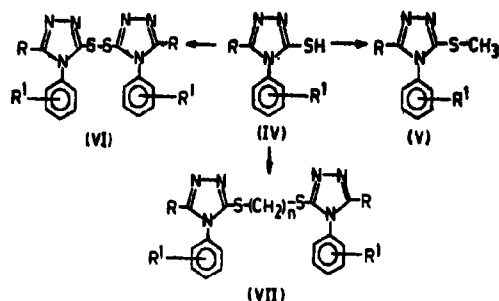
THIOSEMICARBAZIDES have been reported to possess antifungal[1,2], antibacterial[3] and anticonvulsant[4] properties. 2-Amino-5-substituted-1,3,4-oxadiazoles were prepared as antimitotic[5] and muscle relaxant and tranquilizing agents[6]. Substituted thiadiazoles are known to exhibit fungicidal[7], bactericidal[8], herbicidal[9] and insecticidal[10] activities.

Compounds containing triazole ring have shown good fungicidal[11], bactericidal[12] and pesticidal[13] activities. Anticancer and antifungal activities have been displayed by some heterocyclic sulphides[14]. Further, sulphides have been found to be more active than parent mercapto compounds[15]. In view of these, the title compounds have been synthesised.

1-Aryloxy/aryl acetyl-4-aryl thiosemicarbazides (I) have been prepared by the reaction of aryloxy/aryl acetyl hydrazine[16] and aryl isothiocyanate. I was cyclised into 2-arylamino-5-aryloxy/aryl methyl-1,3,4-oxadiazoles (II) in the presence of mercuric oxide. Reaction of I with sulphuric acid gave 2-arylamino-5-aryloxy/aryl methyl-1,3,4-thiadiazoles (III).

(III) (I) (II)

3-Aryloxy/aryl methyl-4-aryl-5-mercapto-1, 2, 4-triazoles (IV) have been obtained by reacting aryloxy/aryl acetyl hydrazine[16] with aryl isothiocyanate in the presence of alkali. Reaction of IV with methyl iodide gave methyl triazolyl sulphides (V) whereas with bromine, *bis*-triazolyl disulphides (VI) and with alkylene dihalide, *bis*-triazolyl alkylene disulphides (VII) were produced.

(VI) (IV) (V)

(VII)

The compounds thus prepared are given in Tables 1-5 along with their antifungal data. Satisfactory N and S analyses results were found for all the compounds

Experimental

All melting points are uncorrected.

Aryloxy/aryl acetyl hydrazines: These were prepared by the method of Conti[16].

1-Aryloxy/aryl acetyl-4-aryl thiosemicarbazides (I): These were prepared by the method of Paul and Basu[17].

2-Arylamino-5-aryloxy/aryl methyl-1,3,4-oxadiazoles (II): 1-Aryloxy/aryl acetyl-4-aryl thiosemicarbazide (0.01 *M*) was dissolved/suspended in methanol and mercuric oxide (0.011 *M*) was added to it. The contents were refluxed for 2 hr and the mixture filtered hot. The filtrate was evaporated and the solid obtained was recrystallised from aqueous ethanol.

2-Arylamino-5-aryloxy/aryl methyl-1,3,4-thiadiazoles (III) : 1-Aryloxy/aryl acetyl-4-aryl thiosemicarbazide (0.01 *M*) was dissolved with cooling in conc. sulphuric acid (10 ml). The solution was kept at room temperature for 2 hr, stirred at intervals and then poured over crushed ice. It was stirred well and left as such for 1 hr. The residue was filtered, washed with water and recrystallised.

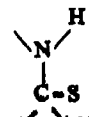
3-Aryloxy/aryl methyl-4-aryl-5-mercapto-1,2,4-triazoles[17] (IV) : A mixture of aryloxy/aryl acetyl hydrazines (0.01 *M*) and aryl isothiocyanate (0.012 *M*) was refluxed in sodium hydroxide solution (20 ml, 8%) for 5 hr, cooled and poured into water. It was stirred and filtered. The filtrate on acidification yielded a solid which was filtered, washed and recrystallised from aqueous ethanol.

Methyl-(3-aryloxymethyl-4-aryl-1,2,4-triazol-5-yl)-sulphides (V) : To a methanolic solution of 3-aryloxy methyl-4-aryl-5-mercapto-1,2,4-triazole (0.01 *M*), fused sodium acetate (2.0 g) and methyl iodide (0.01 *M*) were added. The contents were refluxed for 4 hr, cooled and poured into water. The solid separating out was filtered, washed and recrystallised.

TABLE 1—1-ARYLOXY/ARYL ACETYL-4-ARYL THIOSEMICARBAZIDES (I)

Compd. No.	R	R[1]	m.p. °C	Yield %	Fungicidal activity Conc. 10 ppm	
					A. niger	*H. oryzae*
1[a]	4-Cl-3-CH_3.C_6H_3-O.CH_2	2-OCH_3	180	94	24.4	25.1
2	4-Cl-3-CH_3.C_6H_3-O.CH_2	3,4-$(CH_3)_2$	174	98	18.7	21.3
3	4-Cl-3-CH_3.C_6H_3-O.CH_2	3 4-Cl_2	190	85	27.1	27.9
4	2,4-$(CH_3)_2$.C_6H_3-O.CH_2	2-OCH_3	164	97	19.2	18.8
5	2,4-$(CH_3)_2$.C_6H_3-O.CH_2	3,4-$(CH_3)_2$	162	99	16.7	14.8
6	2-4-$(CH_3)_2$.C_6H_3-O.CH_2	3,4-Cl_2	172	72	21.6	23.4
7	C_6H_5-CH_2	2-OCH_3	105	83	11.9	13.1
8	C_6H_5-CH_2	3,4-$(CH_3)_2$	150	82	–	–
9	C_6H_5-CH_2	3,4-Cl_2	140	76	14.4	16.8
10	2,6-$(CH_3)_2$.C_6H_3-O.CH_2	2-OCH_3	148	86	18.8	20.5
11	2,6-$(CH_3)_2$.C_6H_3-O.CH_2	3,4-$(CH_3)_2$	200	98	–	–
12[c]	2,6-$(CH_3)_2$.C_6H_3-O.CH_2	3,4-Cl_2	150	74	22.4	24.1

IR spectral data ν_{max} in cm^{-1}

	C=S (>N-H, C=S)	N-H stretching	-CO.NH-	=C-O-C-	C-Cl	*Ortho*disubstituted benzene
a	1165	3400	1670	1060 1225	750	760
b	1170	3400	1680	1020 1270	–	Monosubstituted benzene 730
c	1175	3400	1655	1070 1225	710	1,2,3,-Trisubstituted benzene 765

NMR spectral data

c Ar-H 2.1-3.2τ, -CH_2- 5.8τ, -CH_3 7.82τ

TABLE 2—2-ARYLAMINO-5-ARYLOXY/ARYL METHYL-1,3,4-OXADIAZOLES (II)

Compd. No.	R	R[1]	m.p. °C	Yield %	Fungicidal activity Conc. 10 ppm	
					A. niger	*H. oryzae*
13[d]	4-Cl-3-CH_3-C_6H_3-O-CH_2	2-OCH_3	171	54	33 9	35.7
14	4-Cl-3-CH_3.C_6H_3-O CH_2	3-4-$(CH_3)_2$	194	70	22 8	27.8
15	4-Cl-3-CH_3.C_6H_3-O.CH_2	3-4-Cl_2	145	51	36.7	39.1
16	2,4-$(CH_3)_2$.C_6H_3-O.CH_2	2-OCH_3	82	44	31.1	33.2
17	2,4-$(CH_3)_2$.C_6H_3-O.CH_2	3,4-$(CH_3)_2$	130	94	27.1	29.8
18	2,4-$(CH_3)_2$.C_6H_3-O.CH_2	3,4-Cl_2	179	76	32.0	35.1
19	C_6H_5-CH_2	2-OCH_3	196	84	13.9	14.1
20	C_6H_5-CH_2	3-4-$(CH_3)_2$	116	93	–	–
21[e]	C_6H_5-CH_2	3,4-Cl_2	125	83	16.8	16.9
22	2,6-$(CH_3)_2$.C_6H_3-O.CH_2	2-OCH_3	145	60	–	–
23	2,6-$(CH_3)_2$.C_6H_3-O CH_2	3,4-$(CH_3)_2$	194	51	29.0	32.4
24	2,6-$(CH_3)_2$.C_6H_3-O.CH_2	3,4-Cl_2	155	54	35.2	38.0

IR spectral data ν_{max} in cm^{-1}

	=C-O-C, C-O stretching	-NH	Conjugated cyclic -C=N	=C-O-C-	C-Cl	*Ortho*disubstituted benzene
d	1115	3480	1570	1020 1235	790	740
e	1110	3360	1570	1030 1250	730	Monosubstituted benzene 720

TABLE 3—2-ARYLAMINO-5-ARYLOXY/ARYL METHYL-1,3,4-THIADIAZOLES (III)

Compd. No.	R	R¹	m.p. °C	Yield %	Fungicidal activity Conc 10 ppm	
					A. niger	*H. oryzae*
25	4-Cl-3-$CH_3.C_6H_3$-$O.CH_2$	2-OCH_3	190[d]	75	40.1	44.5
26	4-Cl-3-$CH_3.C_6H_3$ $O.CH_2$	3,4-$(CH_3)_2$	210	97	32.0	36.5
27[f]	4-Cl-3-$CH_3.C_6H_3$-$O.CH_2$	3,4-Cl_2	218[d]	98	45.8	48.2
28	2,4-$(CH_3)_2.C_6H_3$-O CH_2	3,4-$(CH_3)_2$	200[d]	90	30.5	34.1
29	2,4-$(CH_3)_2$ C_6H_3-$O.CH_2$	3,4-Cl_2	199[d]	87	36 7	40.0
30	C_6H_5-CH_2	2-OCH_3	252	97	15.2	16 1
31	C_6H_5-CH_2	3,4-$(CH_3)_2$	200	95	—	–
32[g]	C_6H_5-CH_2	3,4-Cl_2	151	98	19.9	21.5
33	2,6-$(CH_3)_2$ C_6H_3-$O.CH_2$	2-OCH_3	208[d]	57	—	–
34[h]	2,6-$(CH_3)_2$ C_6H_3-$O.CH_2$	3,4-$(CH_3)_2$	221	95	32 2	35 0
35	2,6-$(CH_3)_2.C_6H_3$-$O.CH_2$	3,4-Cl_2	234[d]	81	41.4	45 0

IR spectral data ν_{max} in cm^{-1}

	-NH	Conjugated cyclic -C = N-	= C-O-C-	C-Cl	1,2,3-Trisubstituted benzene
f	3470	1605	1030 1250	750	–
h	3440	1625	1035 1275	-	745

NMR spectral data

g Ar-H 2 6-2 8τ, -CH_2- 5.8τ

TABLE 4—3-ARYLOXY/ARYL METHYL-4-ARYL-5-MERCAPTO-1,2,4-TRIAZOLES (IV)

Compd. No.	R	R¹	m.p. °C	Yield %	Fungicidal activity Conc 10 ppm	
					A. niger	*H. oryzae*
36[i]	4-Cl-3-CH_3 C_6H_3-O CH_2	2-OCH_3	160	88	41.0	48 7
37	4-Cl-3-CH_3 C_6H_3-O CH_2	3,4-$(CH_3)_2$	175	75	36 5	42.0
38	4-Cl-3-CH_3 C_6H_3-O CH_2	3,4-Cl_2	161	71	44.3	52 7
39	2,4-$(CH_3)_2$ C_6H_3-O CH_2	2-OCH_3	168	97	34.0	40.6
40[j]	2,4-$(CH_3)_2.C_6H_3$-O CH_2	3,4-$(CH_3)_2$	123	94	31 7	32.0
41	2,4-$(CH_3)_2$ C_6H_3-O CH_2	3,4-Cl_2	189	76	38 5	45.8
42	C_6H_5-CH_2	2-OCH_3	182	79	26.2	28.6
43	C_6H_5-CH_2	3-4-$(CH_3)_2$	110	78	–	–
44[k]	C_6H_5-CH_2	3,4-Cl_2	154	67	28.7	36.0
45	2,6-$(CH_3)_2$ C_6H_3-$O.CH_2$	2-OCH_3	202	88	–	–
46	2,6-$(CH_3)_2.C_6H_3$-O CH_2	3,4-$(CH_3)_2$	228	90	30 4	32.9
47	2,6-$(CH_3)_2$ C_6H_3-$O.CH_2$	3,4-Cl_2	222	67	37.8	44 2

IR spectral data ν_{max} in cm^{-1}

	Secondary -NH	Conjugated cyclic = C = N-	-C = S	= C-O-C-	-SH	C-Cl	*Ortho*disubstituted benzene
i	3100	1600	1160	1040 1235	2580	690	750
j	3150	1500	1130	1035 1250	–	–	–

NMR spectral data

k Ar-H 2.6-3.0τ, -CH_2 5.8τ, -SH 8.75τ

Bis-(*3-aryloxymethyl-4-aryl-1, 2, 4-triazol-5-yl*)-*disulphides* (VI) : To an ice cold methanolic solution of 3-aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazole (0.01 *M*), a cold methanolic solution of bromine (0 005 *M*) was added dropwise with swirling. It was kept as such for 2 hr and then evaporated. The residue obtained was washed successively with water, dilute sodium hydroxide and water and recrystallised.

Bis-(*3-aryloxy/aryl methyl-4-aryl-1,2,4-triazol-5-yl*)-*alkylene disulphides* (VII) : A methanolic solution of 3-aryloxy/aryl-4-aryl-5-mercapto-1, 2, 4 - triazole (0.01 *M*), methylene/ethylene dihalide (0.005 *M*) and fused sodium acetate (2.0 g) was refluxed gently for 3 hr, cooled and poured into water. The solid obtained was filtered, washed and recrystallised from aqueous ethanol.

Fungicidal screening: The compounds were evaluated for their antifungal activity against *Aspergillus niger* and *Helminthosporium oryzae* by agar plate technique[18,19] at three different concentrations viz., 1000, 100 and 10 ppm. Two commercial fungicides, BLITOX 50 WP and MEMCGE, were also tested under parallel conditions to compare the result. The number of replications in each case was three.

Results and Discussion

The compounds screened possess moderate to fairly good antifungal activity against both the

TABLE 5—METHYL-(3-ARYLOXYMETHYL-4-ARYL-1,2,4-TRIAZOL-5-YL)-SULPHIDES (V)

Compd. No.	R	R[1]	m.p. °C	Yield %	Fungicidal activity Conc. 10 ppm *A. niger*	*H. oryzae*
48	2,6-$(CH_3)_2.C_6H_3$-$O.CH_2$	2-OCH_3	63	86	39.8	42.7
49[l]	2,6-$(CH_3)_2.C_6H_3$-$O.CH_2$	3,4-$(CH_3)_2$	Viscous liquid	67	–	–
50	2,6-$(CH_3)_2.C_6H_3$-$O.CH_2$	3,4-Cl_2	99	76	39.0	44.7
	Bis-(3-Aryloxymethyl-4-aryl-1,2,4-Triazol-5-yl)-Disulphides (VI)					
51	4-Cl-3-$CH_3.C_6H_3$-$O.CH_2$	2-OCH_3	121	71	47.8	54.6
52[m]	4-Cl-3-$CH_3.C_6H_3$-$O.CH_2$	3,4-$(CH_3)_2$	157	46	41.3	45.2
53	4-Cl-3-$CH_3.C_6H_3$-$O.CH_2$	3,4-Cl_2	160	50	50.6	56.9
	Bis-(3-Aryloxy/Aryl Methyl-4-Aryl-1,2,5-Triazol-5-yl)-Alkylene Disulphides (VII)					
	n = 1					
54[n]	2,4-$(CH_3)_2.C_6H_3$-O CH_2	2-OCH_3	169	91	44.0	46.8
55	2,4-$(CH_3)_2$ C_6H_3-O CH_2	3,4-$(CH_3)_2$	109	91	36.5	38.7
56	2,4-$(CH_3)_2$ C_6H_3-O CH_2	3,4-Cl_2	205	85	48.5	53.3
	n = 2					
57	C_6H_5-CH_2	2-OCH_3	Semi solid	60	–	–
58	C_6H_5-CH_2	3,4-$(CH_3)_2$	70	70	20.0	21.6
59	C_6H_5-CH_2	3,4-Cl_2	81	71	30.6	31.8
	MEMEGE				83.4	75.8
	BLITOX 50 WP (Commercial fungicides)				73 4	80.0

IR spectral data ν_{max} in cm^{-1}

	Conjugated cyclic -C = N-	-C-O-C-	1,2,3-Trisubstituted benzene	C-Cl
l	1480	1035, 1265	750	
m	1480	1040, 1250	–	715
n	1490	1040, 1250	*Ortho*disubstituted benzene 755	–

fungi. In general, the presence of chlorine and/or methoxy group increases the antifungal activity of the compound. The thiadiazoles (III) are more active than the corresponding oxadiazoles (II) which are relatively more potent than the corresponding thiosemicarbazides (I) Further, the alkyl sulphides display nearly the same level of fungicidal activity as their parent triazoles whereas *bis*-triazolyl disulphides and *bis*-triazolyl methylene disulphides are better than their corresponding triazoles. The highest level of activity in each Table has been shown by compounds Nos 3, 15, 27, 38, 53 which contain 4-chloro-3-methylphenoxy and 3,4-dichlorophenyl moieties.

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Chemical Constituents of *Launaea nudicaulis*: C-13 Nuclear Magnetic Resonance Spectroscopy of Taraxasterenes and Pseudo-Taraxasterenes*

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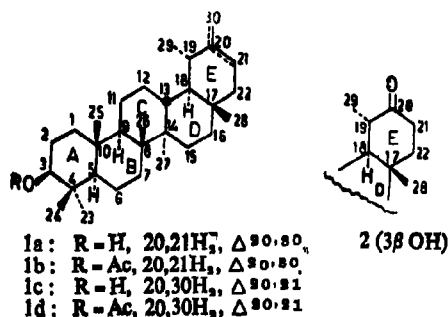
Chemical investigation of *Launaea nudicaulis* yielded β-sitosterol, its acetate and taraxasterol. ^{13}C NMR spectral analyses of taraxasteryl acetate (1b), pseudo-taraxasteryl acetate (1d) and 3β-hydroxy-30-nor-taraxasteran-20-one (2) were made and the diagnostic features are discussed.

PROMPTED by the folk-lore associated with the medicinal properties[1] of *Launaea nudicaulis* (Compositae) we have made a systematic chemical investigation of the plant. This has resulted in the isolation of a triterpenoid and two steroidal constituents, which are identified as taraxasterol, β-sitosterol and its O-acetyl derivative, respectively. The identification is based on their physical constants, spectral data and comparison with authentic samples. In view of a number of recent publications[2-5] on ^{13}C nmr spectral studies on several triterpenoid systems, viz., α- and β-amyrins[2,3], 18,19-oleanenes[4], lupanes[5] and hopanes[5], the isolation of taraxasterol from *L. nudicaulis* in fairly good yield prompted us to carry out detailed ^{13}C nmr spectral analyses of the triterpenoids of taraxasterene and pseudo-taraxasterene types. The present communication while briefly reporting the isolation of the chemical constituents of *L. nudicaulis*, primarily concerns with the results of the ^{13}C nmr spectral analyses.

1a: R = H, 20,21H$_2$, $\Delta^{20,30}$
1b: R = Ac, 20,21H$_2$, $\Delta^{20,30}$
1c: R = H, 20,30H$_2$, $\Delta^{20,21}$
1d: R = Ac, 20,30H$_2$, $\Delta^{20,21}$

2 (3β OH)

The compounds studied for the purpose are the acetyl derivatives of taraxasterol (1a) and pseudo-taraxasterol (1c) and the norketone (2). Pseudo-taraxasteryl acetate (1d) was obtained by treatment of taraxasterol with sulphuric acid followed by acetylation of the product, while the norketone was prepared by the action of OsO_4 on taraxasteryl acetate (1b) followed by periodate oxidation of the resultant 3,20,30-triol. The assignments of the carbon chemical shifts of 1b, 1d and 2 (Table 1) were based on off-resonance decoupling technique indicating substitution profile of carbon centres, functionality manipulation causing predictable shift variations, and comparison with the carbon chemical shifts of appropriate diterpenes[6] (for rings A and B) and triterpenoids[2-5], viz., α- and β-amyrins[2,3] (for rings A and B), lupanes[5] and hopanes[5] (for rings A, B, C and part of D), having some commonness in the carbocyclic systems.

Comparison of the carbon chemical shifts of 1b, 1d and 2 with those of other triterpenoid systems has revealed several distinguishing features. Except the carbon atoms of rings A and B, the carbon chemical shifts of these compounds show practically very little resemblance to those of α- and β-amyrins. This is primarily due to removal of the 12,13-double bond of the amyrins, introduction of the C/D-*trans*, a change over from D/E-*cis* to D/E-*trans* stereochemistry and the structural modification of ring E. This is reflected in the change of chemical shift of C-9 (upfield shift by ~3 ppm) and carbons of C, D and E rings. The most significant is the extraordinary 9-11 ppm shielding of C-27, a characteristic feature also observed in 18,19-oleanenes, the lupanes[5] and the hopanes[5]. While in 18,19-oleanenes this upfield shift of C-27 is due to the removal of δ-effect by C-19 and addition of a γ-effect by C-12, in the case of 1b, 1d and 2 as well as in lupanes and hopanes this may be attributed to the addition of a γ-effect by C-18 and the enhancement of γ-effect by C-12. In fact, the carbon chemical shifts of the compounds under investigation exhibit close resemblance to those of lupanes except C-17 and most of the ring E carbon atoms. The most striking is the chemical shift of C-17 which is shielded by ~ 8.5 ppm compared to the lupanes. This may be attributed to the changed shielding parameters caused by the

* A preliminary account of this work was presented in the "Symposium on Recent Trends in Organic Chemistry", Department of Pure Chemistry, University of Calcutta, 1979, Abstracts of Papers, P. 17, p.37.

replacement of the *trans*-hydrindane system (rings D and E) of lupanes by *trans*-decalin moiety in **1b** (*trans*-octalin and a *trans*-decalone system in **1d** and **2**, respectively).

TABLE 1—CARBON CHEMICAL SHIFT[a] OF **1b**, **1d** AND **2**

	1b	1d	2
C-1	38.7	38.4	38.7
C-2	23.5	23.6	27.3
C-3	80 7	80 8	78 8
C-4	37.6[b]	37 7[b]	38.9[b]
C-5	55.3	55.3	55.3
C-6	18.0	18 1	18 2
C-7	33.8	34 2	33.9
C-8	40 7	41.0	40.8
C-9	50.2	50.2	50 3
C-10	36.9[b]	36.9[b]	37.0[b]
C-11	21.3	21.5	21.1
C-12	25.4[c]	26.9[c]	25 6[c]
C-13	38.3	39.1	37 5
C-14	41 8	42.1	41.7
C-15	26.5[c]	27.5[c]	26 5[c]
C-16	39.2[d]	36.2	36.0
C-17	34.3	34.1	34 1
C-18	48.5	48.6	49 8
C-19	38 2	42 2	46 0
C-20	154.2	139.6	218 0
C-21	25.3[c]	118.8	33.1
C-22	39.0[d]	36.6	36 3
C-23	27.7	27 8	27.9
C-24	16.1[e]	16.2[d]	16.8[d]
C-25	15.7[e]	15.9[d]	15.8[d]
C-26	16.1[e]	16 2[d]	16 2[d]
C-27	14.5	14.6	14.5
C-28	25.0	21.6	21.8
C-29	19.3	17.6	15.3
C-30	107.0	22.4	
-OCOCH$_3$	170.5	170.6	
-OCOC*H*$_3$	21.0	21.3	

[a]The δ values are in ppm downfield from TMS ; δ(TMS) = δ(CDCl$_3$) + 76 9 ppm.
b, c, d, e, Values bearing the same superscript may be interchanged.

Other differences in the chemical shifts of the carbon sites of ring E between these compounds and the lupanes are in conformity with the structural variations of this part of their molecules. The chemical shift assignments for C-29 and C-28 in **1b** are supported by functionality manipulation. Thus, replacement of the exocyclic methylene of **1b** by a C-20 carbonyl function (as in **2**), and the isomerisation of the 20,30-double bond to 20,21-position (**1d**) affect the chemical shifts of both C-29 and C-28, the latter then approaching the value of the corresponding carbon in the lupanes. The reverse assignments for these carbon sites in **1b** would demand an improbable upfield shift (~10 ppm) of C-29 in **2**. Furthermore, in view of the existence of a severe steric interaction[7] between the 29-methyl and the 12-methylene groups, the assigned chemical shift of C-29 appears more logical than otherwise. The differences in the carbon chemical shifts of **1b** and **1d** are only formal and are in accord with those expected from double bond isomerisation.

The results of these spectral analyses thus disclosed diagnostic features which would provide a method for future ^{13}C nmr spectral recognition of new members of the pentacyclic triterpenoids of the taraxasterane and pseudo-taraxasterane types.

Experimental

Isolation of **1a** : Air-dried powdered whole plant (1 Kg) of *L. nudicaulis* was successively extracted with petroleum ether (60-80°), CHCl$_3$ and MeOH. Concentration of petrol extract deposited a white solid (yield 0.06%) which was filtered. The crude solid, on repeated crystallisation from MeOH-CHCl$_3$ (9 : 1) mixture, gave pure **1a**, m p. 221°, $[\alpha]_D$+95.6° (CHCl$_3$); acetate (**1b**), m.p. 239-40°. The filtrate was chromatographed over silica gel using petrol and petrol-EtOAc mixture as eluents. The petrol-EtOAc (20 : 1) eluate on evaporation yielded a further quantity (0.15 g) of **1a**. The petrol-EtOAc (10:1) eluate gave β-sitosterol acetate (yield 0.007%), m. p. 121°, crystallised also from MeOH-CHCl$_3$ mixture Further washing the column with petrol-EtOAc (5 : 1) gave β-sitosterol (yield 0.01%), m.p. 136° ; acetate, m.p. 121° (identical with the natural product). Chromatography of CHCl$_3$ and MeOH extract furnished only traces of **1a** and β-sitosterol.

Isomerisation of **1a** *to* **1c** *and acetylation of* **1c** *to* **1d** : **1a** (0.2 g) was dissolved in a mixture of 10% ethanolic H$_2$SO$_4$ (10 ml) and benzene (10 ml) and refluxed for 5 hr for the double bond isomerisation as reported [7,8] earlier. Solvent was removed under reduced pressure and the residue was diluted with water, extracted with ether, dried and evaporated. Repeated crystallisation of this solid (0.19 g) from MeOH-CHCl$_3$ gave pure **1c**, m.p. 196° ; M$^{\cdot+}$426 ; $\delta_{ppm}^{CDCl_3}$ 1.60, 3H, s and 5.18, 1H, m (*Me*–C=C*H*–CH$_2$–). **1c** was acetylated with Ac$_2$O/Py in the usual manner to give **1d**, crystallised from MeOH–CHCl$_3$, m.p. 228°, $[\alpha]_D$ + 51.8° (CHCl$_3$) ; ν_{max}^{KBr} 1735 and 1250 (OAc) cm^{-1}.

Conversion of **1b** *to* **2** : Following the method reported[7] earlier for structurally similar compound, **1b** (1.9 g) dissolved in a mixture (1 : 1) of dry pyridine and CHCl$_3$ (100 ml) was treated[7] with OsO$_4$ (1 g) and the solution was kept at 20° for 7 days. The solvent was removed under reduced pressure and the dark brown mass was treated[7] with benzene (45 ml), MeOH (45 ml) and a mixture of KOH (10 5 g) and mannitol (10.5 g) in EtOH (45 ml) and water (28 ml), and refluxed for 3 hr. Removal of solvent under reduced pressure left a residue which was diluted with water, extracted with ether and dried. The ether extract, on evaporation, gave a solid which was chromatographed over silica gel. The petrol-EtOAc (1 : 1) eluate gave a crude mass of triol (0.75 g) which was dissolved in EtOH (320 ml) and treated[7] with a solution of sodium *meta*-periodate (0.55 g) in water (5.5 ml). The mixture was kept at 20° for 16 hr. EtOH was removed under reduced pressure and the residue was diluted with water, extracted with ether, dried and evaporated. The solid (0.47 g), on repeated crystallisation from petrol-EtOAc, gave pure **2**, m.p. 260°. (Found : C, 81.2 ; H, 11.24. C$_{29}$H$_{48}$O$_2$ requires C, 81.30 ; H, 11.21%). $\nu_{max}^{CHCl_3}$ 3380 (OH) and 1700

(>C=O) cm^{-1} ; $\delta_{ppm}^{CDCl_3}$ 3.15, 1H, m ($-\overset{|}{C}H-OH$), 2.40, 3H, m ($Me-\underset{|}{C}H-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-$), 1.1, 3H, d, J 7 Hz ($Me-\underset{|}{C}H-\underset{\underset{O}{\|}}{C}-$), 0.71–1.0 ($6-\overset{|}{\underset{|}{C}}-CH_3$) ;

m/e (relative abundance) : 428 (M^+, 17.5), 410 (63.5), 395 (40.9), 367 (25.1), 341 (10.7), 328 (29.3), 259 (10.8), 207 (41), 189 (100), 136 (77 8), 135 (76.3), 123 (60.6), 121 (64.7), 109 (55.5), 95 (77.9), 81 (65.9), 69 (61.8), 55 (55.3) and 43 (45.7).

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Study of Saponins from *Albizzia lebbek* Benth Flowers

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Albizzia lebbek **Benth flowers yield a number of saponins named as lebbekanin-D, F, G and H. They are all glycosides of echinocystic acid with varying sugars. On the basis of enzymatic, partial alkaline hydrolysis, methylation and periodate oxidation studies, partial structures have been assigned to these saponins.**

ALBIZZIA lebbek Benth commonly known as *Siris* belongs to the family Leguminoseae. Varshney *et al*[1-8] have studied various parts of this tree and isolated eight new saponins named as lebbekanin A, B, C, D, E, F, G and H. The present paper describes the study of lebbekanin D, F, G and H, isolated from the flowers of this plant.

Air dried flowers, after defatting with light petroleum ether, were exhaustively extracted with ethanol. The ethanol extract on concentration and usual treatment[1] yielded a light brown substance which gave all the tests for triterpenic saponins.

The crude saponin was then separated into 4 pure saponins, lebbekanin D, F, G and H by repeated column chromatography on silica gel, lebbekanin D being the major part of the mixture.

Study of lebbekanin D: Lebbekanin D, m.p. 217-18°, $[\alpha]_D$-27.5°, (MeOH, c, 1%), R_f 0.350(chloroform : methanol : water 65 : 40 : 10), on acid hydrolysis with 2*N* aqueous sulphuric acid gave echinocystic acid (3β,16 α-dihydroxy olean-12-ene-28 oic acid) (20.1%), and a mixture of five sugars, glucose, galactose, arabinose, xylose and rhamnose in the molar ratio 2 : 2 : 5 : 3 : 3.

Lebbekanin D on alkaline hydrolysis with 5% methanolic potassium hydroxide solution gave a prosapogenin-D_1 and an oligosaccharide-D_1 indicating the presence of ester linkage in the lebbekanin D (i.e. attachment of sugars at C-28 COOH group also). The attachment of sugars at C-16 OH group is not possible due to its strongly hindered position showing thereby that all the sugars are attached at C-3 OH and C-28 COOH groups. The oligosaccharide-D_1 on complete hydrolysis gave glucose, galactose and rhamnose in the molar ratio 1 : 1 : 3. The prosapogenin-D_1 on complete hydrolysis with 2*N* aqueous sulphuric acid gave four sugars, glucose, galactose, arabinose and xylose in the molar ratio 1 : 1 : 5 : 3 and echinocystic acid as genin.

Lebbekanin-D on mild alkaline hydrolysis with 2% methanolic KOH gave prosapogenin-D_2 and oligosaccharide-D_2. Prosapogenin-D_2 on complete hydrolysis with 2*N* aqueous sulphuric acid gave same four sugars glucose, galactose, arabinose and xylose and a neutral genin, m.p. 210-13°, $[\alpha]_D$ +36.9° (EtOH, c, 1%), R_f 0.726, in place of echinocystic acid, m.p. 308-8°, R_f 0.414 (benzene : acetone 6 : 1) isolated by the hydrolysis of prosapogenin D_1. Oligosaccharide D_2 on complete hydrolysis gave the same three sugars i.e., glucose, galactose and rhamnose.

The neutral genin thus obtained (m.p. 210-13°) gave positive tests for triterpenic sapogenins and a double bond. The spectral studies [IR$^{KBr}_{max}$: ν 1700-1720 cm^{-1} (s) ($COOCH_3$); nmr ($CDCl_3$): 3.8 (s) (3H; $COOCH_3$), 5.5 (s) (1H; olifinic), 4.6 (s) (2H; OH)] showed it to be methyl ester of echinocystic acid. The above spectral data tally with the reported data[9] of methyl ester of echinocystic acid. The identity was also confirmed by co-tlc and m.m.p. with an authentic sample of the ester.

This led to the conclusion that glucose, galactose and rhamnose (1 : 1 : 3) are attached to C-28 COOH group as ester and when lebbekanin D is reacted with 2% methanolic KOH the sugars from the C-28 COOH group are knocked out and methyl group from methanol gets attached to COOH at C-28, giving methyl ester of echinocystic acid as neutral genin.

One strange thing is noted. When hydrolysis of lebbekanin-D is carried out with 5% methanolic KOH no methylation takes place at C-28 COOH group or if it takes place, the methyl group is knocked out by the strong concentration of KOH in alkaline hydrolysis and a potassium salt of echinocystic acid is formed. The 2% methanolic KOH, on the contrary, is not sufficient to remove the methyl group and formation of potassium salt of echinocystic acid is not possible (Fig. 1).

2% KOH / MeOH — 5% KOH / MeOH

PROSAPOGENIN - D_2 — LEBBEKANIN - D — PROSAPOGENIN - D_1

2 N H_2SO_4 — 2 N H_2SO_4 — 2N H_2SO_4

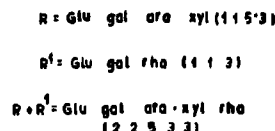
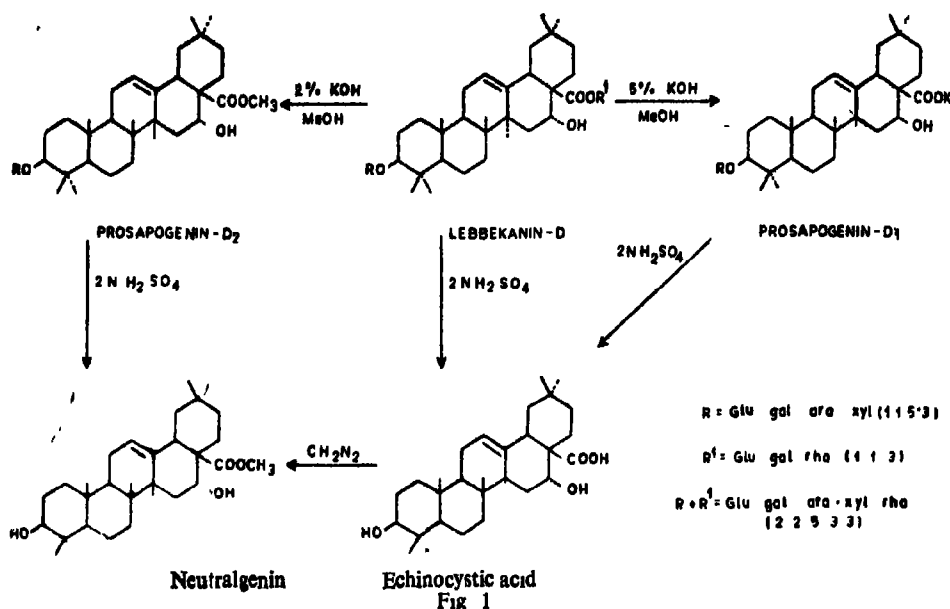
CH_2N_2

R = Glu gal ara xyl (1 1 5 3)

R^1 = Glu gal rha (1 1 2)

R + R^1 = Glu gal ara xyl rha (2 2 5 3 2)

Neutralgenin — Echinocystic acid

Fig 1

Prosapogenin-D_1 and oligosaccharide D_1, obtained on 5% methanolic KOH hydrolysis were separated and their methylation, partial hydrolysis, enzymatic hydrolysis, periodate oxidation were carried out.

Study of prosapogenin-D_1 : Prosapogenin-D_1, m.p. 205-8°, $[\alpha]_D$-24.3° (meOH c, 1%), R_f 0.46 (chloroform, methanol : water 65 : 40 : 10), on acid hydrolysis with 2*N* aqueous sulphuric acid gave echinocystic acid and a mixture of four sugars, glucose, galactose, arabinose and xylose in molar ratio 1 : 1 : 5 : 3.

In order to find out the attachment and sequence of the sugars, prosapogenin-D_1 was methylated by Hakomori's method[10] followed by two Purdie methylation[11] in order to ensure complete methylation (checked by ir spectra). Fully methylated prosapogenin was subjected to methanolysis with 3% methanolic hydrogen chloride. The resulting methylglycoside of methylated sugars obtained were identified by glc on 8% OS-138 on chromosorb W column (NAW), relative retention times were determined taking methyl 2,3,4,6-tetra-O-Methyl α-D glycosides as reference. Following methylglycosides of methylated sugars were tentatively identified :

(i) Methyl-2,3,4-tri-O-methyl-β-D-xyloside.

(ii) Methyl-2,3,5-tri-O-methyl-α-L-arabinoside.

(iii) Methyl-3,4-di-O-methyl-β-D xyloside.

(iv) Methyl-2,3,4,6-tetra-O-methyl-α-D-glucoside.

(v) Methyl-3-O-methyl-α-L-arabinoside.

(vi) Methyl-2-O-methyl-α-L-arabinoside.

(vii) Methyl-2,3,6-tri-O-methyl-α-D-galactoside.

Prosapogenin-D_1 on partial hydrolysis with 0.1*N* aqueous sulphuric acid on water bath for 1 hr gave three sugars, glucose, arabinose and xylose but galactose was not liberated. This showed the back bone position of galactose. On partial hydrolysis for 1 hr three sugars, glucose, arabinose and xylose were liberated. This indicates that these sugars were linked through weak linkages or had a terminal position in the sugar chain. Presence of methyl ethers of arabinose in methyl sugars shows that the branching is taking place through these molecule.

Prosapogenin-D_1 was treated with $NaIO_4$ (0.5*M*), oxidised prosapogenin was extracted with *n*-butanol and was hydrolysed. The hydrolysate showed the presence of only arabinose. It confirms that branching is taking place through arabinose and also support the methylation results.

Study of oligosaccharide D_1 : Oligosaccharide D_1 was completely methylated by Hakomori's method followed by one Purdie methylation. Complete methylation was checked by ir spectra. Methylated oligosaccharide was subjected to methanolysis in the usual manner. The methyl glycosides of methylated sugars obtained were identified by glc under similar conditions. Following methylglycosides of different methyl sugars were identified :

(i) Methyl-2,3,4-tri-O-methyl-α-L-rhamnoside.

(ii) Methyl-3,4-di-O-methyl-α-L-rhamnoside.

(iii) Methyl-2,3,6-tri-O-methyl-α-D-glucoside.

(iv) Methyl-2,3-di-O-methyl-α-D-galactoside.

Methylation results showed that the two rhamnose molecules have terminal positions whereas glucose, galactose and one rhamnose are present in the back bone position. Branching is taking place through galactose molecule as it comes as 2,3-di-O-methyl-α-D-galactose.

Enzymatic hydrolysis of lebbekanin-D with β-glucosidase did not liberate any sugar indicating the absence of β-glycosidic linkage in the glucose molecule.

Since the attachment of sugars at C-16 OH group is not possible due to its strongly hindered position, the only possibility that remains is of C-3 OH group

which is the usual position for the attachment of sugars[1] in the case of triterpenic saponins. Thus, lebbekanin-D has two sugar chains, one attached to the C-28 COOH group and other at the C-3 OH group.

On the basis of above results partial structure of lebbekanin-D may be assigned as structure (I).

Study of lebbekanin-F: Lebbekanin F, m.p. 204-5°, $[\alpha]_D$-40° (MeOH c, 1%), R_f 0.453, on acid hydrolysis with 2*N* aqueous sulphuric acid gave an acid genin (24.5%). It has been identified as echinocystic acid by direct comparison.

The hydrolysate obtained was neutralized and deionised and on paper chromatography showed the presence of five sugars identified as glucose, arabinose, xylose, fucose and rhamnose present in the molar ratio 2 : 2 : 2 : 1 : 3.

Lebbekanin-F on alkaline hydrolysis with 5% methanolic/KOH on boiling water bath gave prosapogenin-F and oligosaccharide-F, indicating the presence of ester linkage in saponin i e attachment of sugars at C-28 COOH group.

Oligosaccharide-F on complete hydrolysis gave three sugars identified as glucose, xylose and rhamnose. *Prosapogenin-F* on complete hydrolysis gave five sugars glucose arabinose, xylose, fucose and rhamnose.

Lebbekanin-F on partial hydrolysis with 0.1*N* sulphuric acid for 1 hr gave four sugars, glucose, arabinose, xylose and rhamnose only. On enzymatic hydrolysis with β-glucosidase, it did not liberate any sugar indicating the absence of β-linkage.

Since the attachment of sugar at C-16 OH groups is not possible due to its strongly hindered position, all the sugars are attached at C-3 OH and C-28 COOH groups.

On the basis of above results lebbekanin-F has been assigned structure (II).

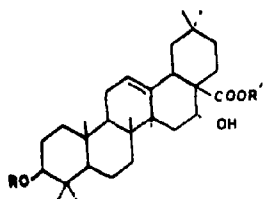



Fig. 2

(I) R+R' = Glu : gal : ara : xyl : rha. (2 : 2 · 5 : 3 : 3)
R = Glu : gal : ara : xyl (1 : 1 : 5 · 3)
R' = Glu : gal · rha (1 . 1 : 3)

(II) R+R' = Glu : ara : xyl : fuc. rha. (2 : 2 : 2 : 1 : 3)
R = Glu : ara : xyl : fuc. rha
R' = Glu : xyl : rha.

(III) R+R' = Glu : ara : xyl : fuc. rha. (3 : 2 : 2 : 2 : 3)
R = Glu : ara : xyl : fuc · rha
R' = Glu : xyl : rha.

(IV) R+R' = Glu : gal : ara : xyl : rha. (4 : 2 : 3 : 3 : 3)
R = Glu : gal : ara : xyl
R' = Glu : gal : rha.

Study of lebbekanin-G: Lebbekanin-G, m.p. 210-12°, $[\alpha]_D$-38.5° (MeOH c, 1%), R_f 0.390, on acid hydrolysis with 2*N* H_2SO_4 gave an acid genin (18%) which was identified as echinocystic acid and five sugars glucose, arabinose, xylose, fucose and rhamnose present in the molar ratio 3 : 2 : 2 : 2 : 3.

Lebbekanin-G on alkaline hydrolysis with 5% methanolic KOH gave prosapogenin-G and oligosaccharide-G indicating the presence of ester linkage i.e. attachment of sugars at C-28 COOH group.

Oligosaccharide-G on complete hydrolysis gave three sugars glucose, *xylose and rhamnose. Prosapogenin-G on complete hydrolysis gave five sugars, glucose, arabinose, xylose, fucose and rhamnose.*

Lebbekanin-G on partial hydrolysis with 0.1N H_2SO_4 gave glucose and rhamnose after 1 hr and glucose, arabinose, xylose and rhamnose after 2 hr while on enzymatic hydrolysis with β-glucosidase, did not liberate any sugar indicating the absence of β-linkage.

On the basis of above results lebbekanin-G has been assigned the structure (III).

Study of lebbekanin H: Lebbekanin-H, m.p. 220-22°, $[\alpha]_D$-27.13° (MeOH c, 1%), R_f 0.324, on acid hydrolysis with 2*N* H_2SO_4 gave an acid genin (15.5%) identified as echinocystic acid and five sugars glucose, galactose, arabinose, xylose and rhamnose, present in the molar ratio 4 : 2 : 3 : 3 : 3.

Lebbekanin-H on alkaline hydrolysis with 5% methanolic KOH gave prosapogenin-H and oligosaccharide-H showing the presence of ester linkage in saponin i.e attachment of sugars at C-28 COOH group.

Prosapogenin-H on complete hydrolysis gave four sugars glucose, galactose, arabinose and xylose while oligosaccharide-G gave three sugars glucose, galactose and rhamnose

Lebbekanin-H on partial hydrolysis with 0.1*N* H_2SO_4 gave glucose and rhamnose after 1 hr. On enzymatic hydrolysis with β-glucosidase no sugar was liberated showing the absence of β-linkage.

On the basis of above results lebbekanin-H has been assigned the structure (IV)

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A New Reagent System for Photometric Analysis of Selenium in Complex Materials

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A new reagent system consisting of 4-nitrophenyl hydrazine and 8-quinolinol is described for the photometric determination of selenium. 4-Nitrophenyl hydrazine is oxidised with selenious acid in 6 *M* hydrochloric acid to 4-nitrophenyl-diazonium chloride which is then coupled with 8-quinolinol to form an 'azoxine' dye. The dye gives intense purple colour in alkaline medium with an absorption maxima at 550 nm. The colour system obeys Beer's law in the range of 7-45 μg Se/25 ml. The molar absorptivity and Sandell's sensitivity are 3.2×10^4 l. mole^{-1} cm^{-1} and 0.0025 μg/cm^2 respectively. The optimum reaction conditions and other analytical parameters are evaluated. The effect of various ions is discussed. The method is applied for detection and determination of selenium in complex materials such as cabbage leaf and cigarette paper.

SELENIUM and its compounds are of wide occurrence and known for their toxicity[1]. Selenium may be inhaled as fumes, dust or absorbed through skin and gastrointestinal tract. When taken into body, it is rapidly absorbed in blood and gets accumulated in lower kidney and muscle tissue. Several reports list selenium as a carcinogen[2,3]. Intoxication due to increased dietary intake of selenium has been reported to cause bad teeth, jaundice, chlosema, vertigo, chronic gastrointestinal disorder, dermititis, hair loss, fatigue, etc[4]. Intake of selenium bearing plants causes chronic selenosis. It has been found that cruciferous plants accumulate much more selenium than other vegetables[5]. Selenium is also reported to be present in cigarette paper and tobacco[6-8]. These materials are largely consumed. Hence, sensitive methods are required for analysis of selenium in these materials.

Several analytical methods have been proposed for determination of selenium and they have been nicely reviewed[9-11]. Most popular spectrophotometric methods for determination of selenium are based on preparing sol of selenium and subsequent measurement of absorbance of the colloidal solution. Different reducing agents and stabilising agents have been proposed[12]. The methods are less sensitive and less specific. Other methods are based on the formation of complexes with *o*-diamines which form coloured or fluorescent paizselenol with selenious acid[13,14]. These methods lack sensitivity and selectivity. Some other methods make use of oxidising property of selenious acid[15]. The present investigation is based on oxidation of 4-nitrophenyl hydrazine to 4-nitrophenyl diazonium chloride with selenious acid in strong hydrochloric acid which is then coupled with 8-quinolinol in alkaline medium. The violet coloured dye is measured photometrically at 550 nm. The optimum reaction conditions and other analytical parameters are evaluated. The method has been successfully used for the analysis of selenium in cigarette paper and cabbage leaves.

Experimental

Apparatus and reagents : All spectrophotometric measurements were done at ECIL spectrophotometer model GS-865 and Carl Zeiss Spekol using 1 cm matched silica cells. An ECIL *p*H meter model 821 was used for *p*H measurements. A thermostated water bath was used for maintaining constant temperature.

The stock solution of selenium (1 mg/ml) was prepared by dissolving 0.22 g of sodium selenite in 100 ml distilled water. Working standards were prepared by appropriate dilution. 0.02% solution of 4-nitrophenyl hydrazine (4-NPH) in water and 0.2% solution of 8-quinolinol in 90% ethanol were used.

Procedure : An aliquot of sample solution (not more than 4 ml) containing 7-45 μg of selenium was transferred to a test tube. To it was added 1 ml of 4-NPH and the acidity was maintained around 6*M*. The test tube was kept at 60±2° for 15 min in the thermostated water bath and the contents were transferred to a 50 ml beaker. To it was added 1 ml of the 8-quinolinol solution, 1 ml of 10% solution of disodium EDTA and 1 ml of 10% solution of sodium potassium tartrate and mixed well. The mixed solution was made alkaline by adding 5 *M* sodium hydroxide solution drop by drop, cooling it simultaneously to 25° to prevent the decomposition of the dye by the heat produced during neutralisation. The violet dye was transferred into a 25 ml volumetric flask and diluted to the mark with distilled water. The absorbance of this solu-

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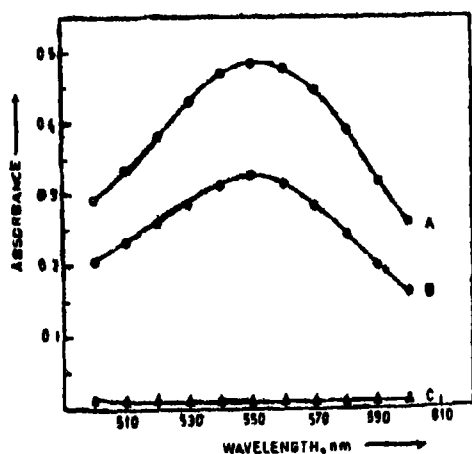
was measured at 550 nm and the amount of nium was calculated from a calibration curve.

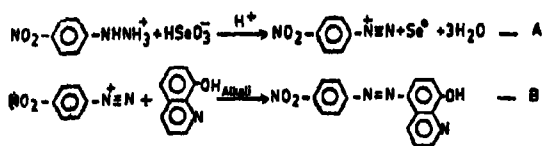
Preparation of sample solution : Into a 100 ml dahl flask 1 g of dried crushed cabbage leaf/ rette paper from 5 cigarettes was taken and to as added 15 ml concentrated nitric acid. The tion was heated till reduced to 2-3 ml. This edure was repeated for 3-4 times to ensure plete decomposition. Then 5 ml of conc. hydroric acid was added and heated till 2-3 ml was This procedure was also repeated 2-3 times emove nitrous fumes. The digest was filtered, if ssary, and the volume was made upto 10 ml distilled water. Selenium content was detered by the recommended procedure. Precaution t be taken to see that mixture does not dry up pletely during digestion, otherwise there will be of selenium through volatilisation of oxides selenium[16]. It was found that samples of bage had no selenium, therefore known amount elenium was added to the sample before diges- . Selenium content was then determined by the mmended procedure. As concentrated nitric acid hydrochloric acid was found to give nearly ise results, under the condition employed, the of perchloric acid[17,18] was avoided for the ons of safety. However, when perchloric acid used, the results obtained were high, since ants interfere with this method.

lts and Discussion

pectral characteristics : Absorption spectra of ent and azoxine dye are shown in Fig. 1. The shows λ_{max} at 550 nm. The reagent has negligi- absorption at this wavelength. However, a ent blank was used to compensate for any ge in the colour of the reagent on storage.

. Absorption spectra of azoxine dye and reagent blank in alkaline medium against water.
A. Se – 30 μg/25 ml.
B. Se – 20 μg/25 ml.
C. Reagent black.

eaction : The reaction is given below. The ion B is identical with the reaction proposed by and Gupta[19].

$$NO_2-C_6H_4-NHNH_3^+ + HSeO_3^- \xrightarrow{H^+} NO_2-C_6H_4-\overset{+}{N}\equiv N + Se^0 + 3H_2O \quad — A$$

$$NO_2-C_6H_4-\overset{+}{N}\equiv N + \text{8-quinolinol} \xrightarrow{\text{Alkali}} NO_2-C_6H_4-N{=}N-\text{(8-hydroxyquinolyl)} \quad — B$$

Effect of variables :

Acidity : The effect of acidity on oxidation of 4-NPH was studied by maintaining different molarities of hydrochloric acid ranging from 1 to 7 *M* and developing the colour by the recommended procedure. This revealed that atleast 5 *M* hydrochloric acid was required for complete oxidation. Constant absorbance values were obtained when the acidity was above this. It was also found that wave length of maximum absorption remains constant in the range of acidity.

Effect of time, temperature and reagent concentration : The oxidation reaction is dependent on temperature. To determine the effect of temperature and time, the reaction was carried out at temperatures varying from 25 to 60°. The maximum time required for complete oxidation and stability of the diazonium chloride at respective temperature were evaluated by carrying out the oxidation reaction for different time and developing the colour. It was found that higher temperature accelerates the reaction, as the same intensity of colour is reached in 10 min at 60°, but in 45 min at 25°. However, the stability of diazonium chloride decreases at higher temperature. In this investigation the reaction was carried out at 60±1° for 15 min.

The amount of reagent is not critical. For 7-45 μg of selenium per 25 ml, 1 ml of 4-NPH and 1 ml of 8-quinolinol gave reproducible results. At higher concentration 4-NPH itself gave colour with sodium hydroxide and it should be avoided.

Effect of pH *and stability of dye :* It was found that for coupling reaction *p*H 11 is required to attain maximum absorbance. This *p*H was attained with 5 *M* sodium hydroxide.

The dye was stable for 3-4 hr. Some turbidity was observed after this period.

Beer's law, molar absorptivity and Sandell's sensitivity : Beer's law was obeyed in the range of 7 to 45 μg/25 ml. The molar absorptivity and Sandell's sensitivity were 3.2×10^4 l. mole^{-1} cm^{-1} and 0.0025 μg/cm^2 respectively. The detection limit was 0.1 μg/ml. The standard deviation and relative standard deviation were ±0.0026 and ±0.814%, respectively.

Validity of the method : To check the validity of the method, 20 μg of selenium was determined in presence of known amounts of interferants. 100 fold excess of Br^-, CN^-, CNS^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, citrate and tartrate, 50 fold excess of Be^{2+}, Ba^{2+}(a), Co^{2+}(a), Ca^{2+}(a), Ni^{2+}(a), Mg^{2+}(a), Zn^{2+}(a), Bi^{3+}(b), Li^+, K^+, Pb^{2+}(a), Al^{3+}(a), 20 fold excess of Te^{4+}, Hg^{2+}(a) and 5 fold excess of Fe^{3+}, Cr^{3+} do not interfere. Many ions (marked by a and b) interfere by precipitation as hydroxide. These are masked with 1 ml of 10% disodium salt of EDTA (a) and

1 ml of 10% sodium potassium tartrate (b), respectively. Cu^{2+}, oxidants such as potassium permanganate, potassium dichromate, Fe^{3+} and reductants such as sulfide, thiosulphate, Sn^{2+} interfere. The interference of Cu^{2+} and Fe^{3+} can be eliminated by separating them as their cupferronates[20].

The method was then successfully applied for the analysis of selenium in cabbage leaves (Table 1) and cigarette paper.

TABLE 1—DETERMINATION OF SELENIUM IN CABBAGE LEAVES

Selenium added μg	Selenium found* μg	Recovery %
40	39.00	97.50
20	19.50	97.50
10	9.70	97.00

*Average of three determinations.

Cigarette paper of different brands were found to contain different amounts of selenium. It was also found that the selenium content varied with different lot of the same brand. It was found that even one cigarette paper contained sufficient selenium to give positive test for selenium by this method.

The method is simple, sensitive, free from rigorous control of pH and can be compared favourably with other methods[13-16]. The coupling reagent 8-quinolinol used in proposed method is non-toxic as compared to α-napthylamine used in Kirkbright's method[15]. The method can be applied for the analysis of selenium in complex materials with reproducible results.

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Notes

Inorganic Coordination Complexes. Part-V. Complexes of Divalent Zinc, Cadmium and Mercury with Substituted Salicyl Hydrazines

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As a part of our studies on metal complexes[1-6], we report here the reactions of divalent Zn, Cd and Hg with N-salicyl hydrazine (SH), N-N'-disalicyl hydrazine (DSH), N-acetyl-N'-salicyl hydrazine (ASH) and N-benzoyl-N'-salicyl hydrazine (BSH). Various substituted acyl hydrazines have been reported to coordinate through >C=O and $-NH_2$ groups[7-9], but the complexes of SH, DSH, ASH and BSH described here are of particular interest as -OH group formed by the enolization of these hydrazines provides an additional coordination site for various metal ions.

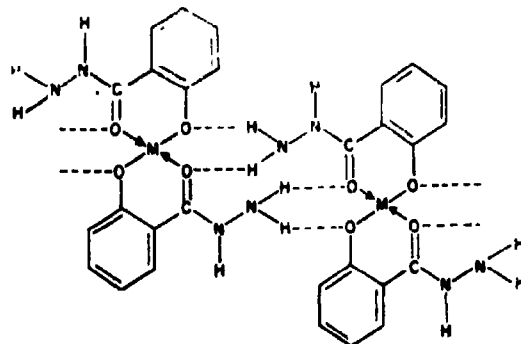
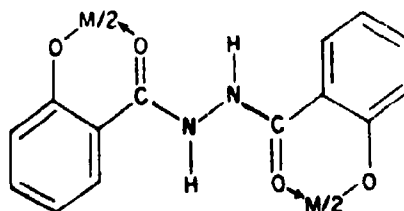
Experimental

SH was prepared by the reaction of methyl salicylate and hydrazine hydrate[10-11]. ASH and BSH were obtained by acetylation and benzoylation of SH, whereas DSH was prepared by heating a mixture of methyl salicylate and SH. All ligands were further purified by repeated crystalization from hot ethanol. The complexes were prepared by the method described earlier[4].

Results and Discussions

The insolubility of the complexes under investigation in most of the organic solvents indicated their polymeric nature[11] (cf. I, II and III). The low molar conductance values of the complexes (varying from 0.6-1.0 mhos) in pyridine showed them to be non electrolytes. All the complexes are thermally stable, as they decompose above 200° without melting.

1. *SH and DSH complexes* : The ir spectra have been interpreted on the basis of published data[12-13]. On comparing the spectra of ligands with the spectra of the complexes, a considerable negative shift of 40-60 cm^{-1} in C=O stretching frequency indicates the coordination of ligands through oxygen of C=O group. Coordination through nitrogen has been ruled out as δ NH mode remains uneffected. However, the negative shift of 15-25 cm^{-1} observed in the ring stretching vibrations and disappearance of OH frequency in the spectra of complexes confirm the coordination of ligand through oxygen atom of carbonyl group and oxygen of the phenolic group after deprotonation[4]. Similar ir spectral features have been observed with slight alteration in number, position and intensity of bands in the DSH complexes.

The following polymeric structures, I and II, have been proposed for SH and DSH complexes, respectively.

I
[M = Zn, Cd, Hg]

II
[M = Zn, Cd, Hg]

2. *ASH and BSH complexes* : Ohta reported that acyl hydrazines show keto-enol tautomerism[14]. In view of this, ASH and BSH may exist as

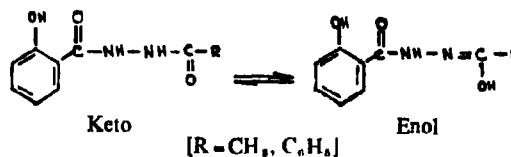
Keto ⇌ Enol
[R = CH_3, C_6H_5]

The spectra of the complexes showed the negative shift of about 50 cm^{-1} in the band around 3300 cm^{-1} as compared to the spectra of the ligands showing involvement of NH group in complexation through nitrogen. An intense band in the region 1610-1670 cm^{-1} in the spectrum of ligand has been assigned to the amide I (C=O) mode. But in the complexes, a band is observed around 1600 cm^{-1} which suggests that the amide I band of the ligand either suffers a negative shift or disappears due to formation of C=N as a results of enolization. This has been further substantiated by a band around 1500 cm^{-1} due to involvement of NCO group in complexation[15]. The appropriate M-N and M-O frequencies are listed in Table 1. Variation in M-N stretching frequencies of these complexes follows the "Irving Williams" order of stability of the bivalent metal complexes[16] i.e. Zn > Cd > Hg.

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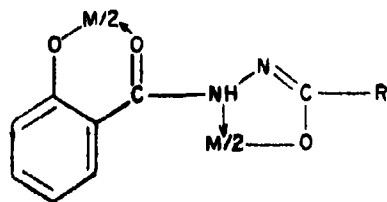
TABLE 1—ANALYTICAL AND SPECTRAL DATA OF Zn, Cd AND Hg COMPLEXES OF SUBSTITUTED SALICYL HYDRAZINES

(Values in parenthesis are calculated)

Compounds	m.p./ Dec. Temp. °C	Colour	Metal %	C %	H %	N %	IR spectral data in cm^{-1} NH and OH	C=N, C=O	M–N	M–O
SH	144	White	–	55 02 (55.17)	5.15 (5.14)	18.20 (18.40)	3330m 3280s	1630s 1600s	–	–
$Zn(SH\text{-}H)_2$	350	Dirty white	17.50 (17.71)	45 92 (45 77)	3.72 (3.81)	15.10 (15.25)	3275s	1580s 1550s	380m	430m
$Cd(SH\text{-}H)_2$	250	Bright white	27.15 (27.05)	40 16 (40.57)	3.41 (3.38)	13.40 (13.52)	3280s	1575s 1550s	350m	440m
$Hg(SH\text{-}H)_2$	200	White	39.68 (39.84)	33 10 (33 46)	2.62 (2.78)	11.20 (11.15)	3275s	1580s 1560s	320m	455m
DSH	302	Yellow	–	61.10 (61.25)	4.25 (4.38)	9.50 (9 69)	3300m 3100s	1610s	–	–
Zn(DSH-2H)	300	Light yellow	19 61 (19.40)	47 63 (47.32)	2 90 (2.81)	8.42 (8.35)	3100s	1560s	375m	435m
Cd(DSH-2H)	285	Yellowish white	29.45 (29.31)	43 43 (43.71)	2.58 (2.61)	7.30 (7.32)	3110s	1565s	340m	440m
Hg(DSH-2H)	248	Light yellow	42.35 (42.55)	35 28 (35 74)	2.01 (2.12)	5.81 (5.95)	3105s	1570s	325m	450m
ASH	183	White	–	55.86 (55 65)	5.15 (5 35)	14.70 (14.40)	3400s 3320s	1670s 1630s	–	–
Zn(ASH-2H)	400	White	25.10 (25.29)	42 21 (42.02)	3 21 (3.11)	10.75 (10.89)	3275s	1610s	370m	440m
Cd(ASH-2H)	350	White	36.68 (36.84)	35 31 (35.52)	2.52 (2.63)	9 10 (9.21)	3270s	1610s	345m	445m
Hg(ASH-2H)	200	White	51.15 (51.02)	29.35 (29.55)	2.10 (2.04)	7 05 (7 14)	3270s	1600s	320m	455m
BSH	280	White	–	65.75 (65.63)	4.96 (4.69)	10.70 (10.94)	3320s	1660s 1610s	–	–
Zn(BSH-2H)	400	Yellowish white	20.45 (20.37)	52.42 (52.66)	3.05 (3.13)	8.65 (8.77)	3280s	1600s	385m	435m
Cd(BSH-2H)	350	,,	30 55 (30.60)	45 71 (45.90)	2.68 (2.73)	7.42 (7.65)	3285s	1605s	350m	445m
Hg(BSH-2H)	200	,,	44.20 (44.05)	37.15 (37 00)	2 18 (2.20)	6.19 (6.16)	3280s	1600s	330m	450m

In view of the very poor solubility of these complexes in most of the organic solvents, the polymeric structure III may be proposed.

III
[M = Zn, Cd, Hg & R = CH_3, C_6H_5]

Acknowledgement

The authors are grateful to Prof. V. S. Misra, Head of Chemistry Department, Lucknow University and to Dr. D. Prakash, Senior Geo-chemist, Directorate of Geology and Mining, U. P., Lucknow for providing laboratory facilities.

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Spectral and Magnetic Studies of Some Mixed Ligand Complexes of High-Spin Cobalt(II)

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DIVALENT cobalt complexes have tendency towards oxidation in presence of a variety of complexing agents[1]. The complexes synthesized in the present study have been found to be sufficiently stable and resistant to oxidation. In these ligand exchange reactions the comparatively weak bonded coordinated water molecules of the parent β-ketoester complexes of Co(II) are quantitatively replaced by thiourea. Since the solubility of these complexes in common organic solvents has been found to be very low, the diffuse reflectance has been carried out using lithium fluoride as diluent as well as reference.

Experimental

Diaquo *bis*-(methylacetoacetato) and diaquo *bis*-(ethylacetoacetato) of Co(II) were prepared by known method[2]. The mixed ligand complexes were synthesized by adding an ethanolic solution of the second ligand viz. thiourea or phenylthiourea (0.02 mole) to an ethanolic solution of diaquo *bis*-(MeAA) Co(II) or diaquo *bis*-(EtAA) Co(II) (0.01 mole). The resulting reaction mixture was refluxed for one and half hour. The complex separated out on cooling, was filtered, washed with ethanol and ether and dried *in vacuo* over anhydrous calcium chloride.

Magnetic measurements were made on a Gouy magnetic balance at $300 \pm 1°$K. The ir spectra of the complexes were recorded on a Perkin-Elmer 577 spectrophotometer in KBr phase while diffuse reflectance spectra were recorded on a VEB Carl Zeiss Jena VSU 2P spectrophotometer using the reflectance attachment o/r.

Results and Discussion

The magnetic moment (μ_{eff}) for all the complexes ranges between 4.95-5.28 B.M. (Table 1) indicating the complexes to be high-spin complexes with three unpaired electrons and having almost octahedral stereochemistry[3,4]. Absence of absorption band around 3450 cm^{-1} in the mixed ligand complexes, discernible in parent complexes, show the replacement of two coordinated water molecules of parent complexes by two thiourea ligands. A considerable overlapping of bands due to coordinated β-ketoesters and the second ligand was observed. Definite shifts were observed in C-O, C-C and M-O stretching frequencies (Table 1) on coordination of thiourea ligands, because all the three bands are involved in the resonance system. The direction of these shifts cannot be correctly predicted since there will be a metal-ligand π bonding superimposed on a ligand-metal bond[5]. The shift of -NH absorption vibration of thiourea ligands towards higher and that of C=S band (around 740 cm^{-1}) towards lower frequency regions suggest the coordination of thiourea or substituted thiourea ligand to the metal through S-atom[6,7].

In high-spin cobalt(II) complexes, the experimentally observed spin-allowed transitions in increasing order of energy are ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, and are denoted as ν_1, ν_2 and ν_3, respectively[8]. By using transitions ν_1 and ν_3, and following weak field coupling scheme, the values for Racah interelectronic repulsion parameter, B, and crystal field splitting energy parameter, 10 Dq, have been calculated[9] and are summarized in Table 1 along with experimentally observed transition energies. In the calculation of the different parameters the transition band ν_2 has not been used since it is a weak band due to two electron jump and hence its accurate location is difficult. The Jahn-Teller effect in the ground state ${}^4T_{1g}$ (F) of octahedral d^7 ion is expected to be weak and has not been considered here. The value of the free gaseous ion, 972 cm^{-1}, is used to calculate the value for nephelauxetic ratio, β. The lower values for β in these mixed ligand complexes as compared to their respective parent complexes indicate the increase in covalency on further complexation. By using the modified Tanabe-Sugano diagram given by Lever [9], the graphical values for parameters B and 10 Dq have been deduced using transition energy ratio ν_3/ν_1 (Table 1).

TABLE 1—EXPERIMENTALLY OBSERVED TRANSITION ENERGIES, VALUES OF VARIOUS PARAMETERS AND IR SPECTRAL DATA (IN cm^{-1})

Complex	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	B	10 Dq	B (Graph)	10 Dq (Graph)	ν_3/ν_1	β	ν(C-O)	ν(C-C)	ν(M-O)
$Co(MeAA)_2(H_2O)_2$	8547	19801	21505	944.7	9759	954.5	9831	2 51	0.97	1620 s	1505 s	450 m
$Co(MeAA)_2(TU)_2$	8333	17842	20619	890.1	9397	902 7	9388	2 47	0.91	1630 s	1490 m	465 m
$Co(MeAA)_2(PTU)_2$	8474	18975	21276	933.8	9676	936.0	9640	2.51	0.96	1580 s	1485 s	468 w
$Co(EtAA)_2(H_2O)_2$	8620	19607	21739	956.8	9853	928.6	9471	2.52	0.98	1626 s	1525 s	480 m
$Co(EtAA)_2(TU)_2$	8488	19157	20408	872.8	9660	871 7	9588	2 40	0 89	1630 s	1530 m	462 m
$Co(EtAA)_2(PTU)_2$	8605	18867	21276	924.5	9831	926.6	9636	2.47	0.95	1547 s	1532 m	468 m

MeAA = methylacetoacetate, EtAA = ethylacetoacetate ; TU = thiourea ; PTU = phenylthiourea.

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[*] For correspondence.

Hay and Cauchley[5] have proposed the *trans* arrangement of the ligand for the β-ketoester derivatives of cobalt(II). Ballhausen *et al*[11] have correlated this *trans* behaviour in cobalt(II) complexes with the width of the electronic absorption bands. The presence of narrow electronic bands was correlated to the *trans* configuration of the complexes. The electronic bands in these mixed ligand complexes also retain the same absorption pattern when the $Co(MeAA)_2(H_2O)_2$ and $Co(EtAA)_2(H_2O)_2$ react with thiourea and the observed bands are not broad. Thus, we can assume that the mixed ligand complexes derived from β-ketoesters of cobalt(II) have also the *trans* configuration with almost octahedral stereochemistry. Slight distortion may be due to the non-identical nature of the coordinating atoms.

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Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-4′-Chloro-2′-Methoxyaniline Complexes with La^{3+}, Y^{3+}, Nd^{3+}, Dy^{3+} and Gd^{3+}

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It has been generally concluded from previous work[1-4] on the correlation between chelate stability and ionic radii that the stabilities of the tripositive lanthanide complexes should increase with decreasing cation radius or increasing atomic number. An examination of the stability constant data generally bears out this expectation but reveals an anomalous behaviour in some instances. A large amount of work done relates to $\bar{O}$, $\bar{O}$ donors. However, complexes containing $\bar{O}$ and N functional groups (azomethines) have not been dealt with very extensively. This communication is a continuation of our work[8] on Schiff bases. The new Schiff base, 2-hydroxy-1-naphthalidene-4′-chloro-2′-methoxyaniline has been selected to study a correlation, if any, between the stability constants and the ionic potentials of the trivalent lanthanides.

Experimental

The ligand 2-hydroxy-1-naphthalidene-4′-chloro-2′-methoxyaniline was synthesised and repeatedly crystallised from alcohol to get an analytically pure sample with m.p. 271° (observed). All reagents were of A. R. grade and their solutions were made in purified dioxan[6] and double distilled CO_2 free water *p*H metric titrations of the following solutions, (i-iii) were carried out at 25±0.1° under nitrogen atmosphere. These solutions, with an initial volume of 40 ml, were titrated with a carbonate free standard sodium hydroxide solution (1.07 *M*) using a Corning Model 12 precision research *p*H meter having an accuracy of 0.005 *p*H unit with combined glass electrode and calomel reference electrode. The medium of titration was 75 : 25 (v/v) dioxan-water mixture. A constant ionic strength (0.1 *M*) was maintained by adding requisite amount of $NaClO_4$.

(i) 5 ml (0.16 *M*) $HClO_4$ + 5 ml (0.64 *M*) $NaClO_4$ + 30 ml dioxan.

(ii) 5 ml (0.16 *M*) $HClO_4$ + 5 ml (0.64 *M*) $NaClO_4$ + 49 84 mg reagent, accurately weighed to give 0.004 *M* reagent concentration in the final solution + 30 ml dioxan.

(iii) 5 ml (0.64 *M*) $NaClO_4$ + 5 ml metal salt (0.008 *M*) solution in (0.16 *M*) $HClO_4$ + 49.84 mg reagent accurately weighed to give 0 004 *M* reagent concentration in the final solution + 30 ml of dioxan.

The experimental method of Irving and Rossotti[7] was applied to find out the values of $\bar{n}$ and *p*L. The titrations were performed in duplicate to test for reproducibility.

Results and Discussion

It may be pointed out here that the ligand used in this study did not undergo hydrolysis under the experimental conditions. This was indicated by rapid attainment of equilibrium during the titrations and by the absence of any significant change in *p*H even after 1 hr. The phenolic OH group of the ligand is deprotonated during complex formation.

From the titration curves of solutions (i) and (ii), $\bar{n}_A$ values at various 'B' values (*p*H meter readings), were calculated and a curve between 'B' and the corresponding $\bar{n}_A$ values was plotted. The value of pK_1^H was evaluated by half integral method as well as from the plot of log $(\bar{n}_A/1-\bar{n}_A)$ vs B. Both these values agree well.

From the titration curves of solutions (ii) and (iii), $\bar{n}$ and pL values were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of metal complex-ion equilibria. The pK_1^H of the ligand and log K_1 and log K_2 of the complexes of Y^{3+}, La^{3+}, Nd^{3+} and Gd^{3+} were evaluated by the half integral method. In the case of dysprosium and praseodymium metal systems, the differences between log K_1 and log K_2 values were found to be less than 1.78 log units and hence the same were evaluated by the least square method. The most representative values are recorded in Table 1. The order of stability of various metal chelates was found to be $Y^{3+} > Gd^{3+} > Nd^{3+} > La^{3+} > Pr^{3+} > Dy^{3+}$.

An attempt to interpret the stability data in terms of an entirely ionic type of bonding in these complexes was unsuccessful as the plot of Z^2/r vs log K_1 values was not linear. The possibility of covalent interaction, however, cannot be completely excluded, as reported in the case of acetylacetone chelates of rare earths[8]. The probable explanation of non-linearity could be that the assumption about ionic character of the metal-ligand bond, on which the linearity relation is based, is not valid. Other probable causes could be possibilities of higher coordination number of metal ion and steric factors.

TABLE 1—STEPWISE STABILITY CONSTANTS OF THE COMPLEXES OF 2-HYDROXY-1-NAPHTHALIDENE-4′-CHLORO-2′-METHOXYANILINE WITH SOME TRIVALENT LANTHANIDES

$t = 25 \pm 0.1°$ $\mu = 0.1$ ($NaClO_4$)

Cations	H^+	Y^{3+}	La^{3+}	Pr^{3+}	Nd^{3+}	Dy^{3+}	Gd^{3+}
log K_1	9.40	9.23	8 72	8.20	9.05	7.59	9.07
log K_2	–	7.08	6.10	6.73	7.05	6.28	6.78

For proton association (H^+), K_1 corresponds to the species LH; while for metal ions, K_1 and K_2 correspond to the species ML_1 and ML_2, respectively.

The standard deviation ranged from 0.05 to 0 1, the limits of error were ± 0.06

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Polarographic Reduction of Uranyl(II) in Presence of Some Disubstituted Pyridines

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THE present paper describes the polarographic reduction of uranyl(II) in presence of some disubstituted pyridines, viz., 2,3-dihydroxypyridine (DPH), 2-amino-3-hydroxypyridine (AHP) and 3-hydroxypyridine-2-thiol (HPT). All the systems show diffusion controlled irreversible reduction waves. Kinetic parameters (αn and $k^{\circ}_{f,h}$) have been calculated and discussed. The ligands contain ideal sites for formation of sterically favoured five-membered ring and provide scope for comparison of donor properties of -OH, $-NH_2$ and -SH groups. Reactions of UO_2(II) with these ligands have been studied earlier pH-metrically[1-3] wherein metal-ligand stability constants were determined.

Experimental

A D.C. manual polarograph with a scalamp galvanometer was used in all investigations. All potential measurements were made with reference to a saturated calomel electrode. The dropping mercury electrode had the characteristics, $m^{2/3} t^{1/6} = 2.054$ mg$^{2/3}$ sec$^{-1/2}$, h=40 cm, t = 3.8 sec. Purified nitrogen was passed through each solution to remove dissolved oxygen. All measurements were carried out at room temperature ($30 \pm 0.1°$).

Reagent grade chemicals were used. Solution of uranyl nitrate was prepared in double distilled water. Stock solutions of DPH and AHP (Aldrich Chemical Co., U.S.A.) were prepared in double distilled water and that of HPT (Fluka AG, Switzerland) in purified methanol. While UO_2(II)-DHP and UO_2(II)-AHP systems were studied in aqueous media, UO_2(II)-HPT system was studied in 30% methanol medium owing to the limited solubility of the ligand in water. Sodium perchlorate was used as the supporting electrolyte and ionic strength was kept constant ($\mu = 0.1$). Acetate buffer was used to maintain the pH. Gelatin (0.003%) was used as the maxima suppressor.

Results and Discussion

Well defined single cathodic waves were obtained in all the three cases. $E_{3/4} - E_{1/4}$ values (69 ± 1 mV) show irreversible nature of the systems and constant values of $i_d/(h_{eff})^{1/2}$ show that the waves are diffusion controlled. Kinetic parameters have been calculated using Oldham and Parry method[4]. According to these authors the equation for an irreversible diffusion controlled wave (at 30°) is

$$-E_{d.e.} = -E_{\frac{1}{2}} + \frac{0.060}{\alpha n} \log\left[\frac{x(5.5-x)}{5(1-x)}\right] \quad \dots (1)$$

where $x = \frac{i_E}{i_{lim}}$, i_E=current at potential E which is valid in the entire region $0 < x < 1$. The plots of $E_{d.e}$ vs $\log\left[\frac{x(5.5-x)}{5(1-x)}\right]$ yield the values of $\frac{0.060}{\alpha n}$ (slope) and $-E_{\frac{1}{2}}$ (intercept). Also, for an irreversible wave the half wave potential is related to the rate constant for the electrode reduction by the expression,

$$E_{\frac{1}{2}} = E_0 + \frac{0.060}{\alpha n} \log\left[0.89\ k^{0}_{f,h}\ \sqrt{(t/D)}\right] \quad \dots \quad (2)$$

where $k^{0\prime}_{f,h}$ is the formal rate constant at a reference potential $E_0 = -0.2412$ volts vs S.C.E. and D and t have their usual significance. The reference potential in the present investigations has been chosen as the normal hydrogen electrode potential (-0.2412 volts vs S.C.E) and the values of $D^{\frac{1}{2}}$ have been obtained using Ilkovic equation. Values of αn and $k^{0}_{f,h}$ have been calculated and presented in Table 1

TABLE 1—KINETIC PARAMETERS

$[UO_2^{2+}] = 1 \times 10^{-4} M$

ligand conc. (mM)	$-E_{\frac{1}{2}}$ (volts vs SCE)	αn	$D^{\frac{1}{2}} \times 10^{3}$ (cm sec$^{-\frac{1}{2}}$)	$k^{0}_{f,h} \times 10^{8}$ (cm^{-1} sec^{-1})
(a) System : UO_2(II)-DHP, pH = 4 4				
2.0	0.460	0.750	2.33	2.71
4.0	0.480	0.742	2.19	1.54
6.0	0.488	0.740	2.03	1.16
8 0	0.492	0 739	1.95	1.01
(b) System : UO_2(II)-AHP, pH = 4.4				
2.0	0.455	0 752	2.41	3.19
4.0	0.476	0.749	2.34	1.52
6.0	0.485	0.752	2.16	1.20
8.0	0 490	0 747	2 17	1 10
(c) System UO_2(II)-HPT, pH = 4.6				
2 0	0 463	0 747	2 18	1 74
4.0	0 481	0 741	2 11	1 46
6.0	0 490	0 740	2 03	1 10
8 0	0 493	0 740	1 86	1 02

A perusal of the results show that the $k^{0}_{f,h}$ values for reduction of UO_2^{2+} in presence of the same concentration of the ligands follow the order HPT < DHP < AHP. Since higher value of the rate constant signifies easier reduction and hence lower stability of the complex, the order of the strength of the metal ligand bond in the complexes of the three ligands appears to be HPT > DHP > AHP.

Uranyl ion falls in the category of hard acids (class 'a') for which the strength of the metal ligand bond should follow the O > N > S order of the donor atoms, so that the order of stability of the complexes formed with the three ligands under study should be DHP > AHP > HPT. For DHP and AHP, the studies were made under similar conditions (both in aqueous media) and the observed behaviour is as expected from theoretical considerations. Deviation in the behaviour of HPT may be because the study was made in 30% methanol medium which has a dielectric constant lower than that of water.

Vlcek[5] also approximated that a complex with a nonhomogeneous coordination sphere will be reduced more easily (i.e., the rate constant for reduction will be higher) than one with fully homogeneous coordination sphere. Consistent with the above, the rate constant for the reduction of the AHP complex is higher than that for the reduction of the DHP complex.

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Determination of Stability Constants of 2-Hydroxy-1-naphthalidene-Sulphamethoxazole Complexes with Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Mg^{2+}

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IN the present investigation, potentiometric studies have been carried out on 2-hydroxy-1-naphthalidene-sulphamethoxazole and its complexes with some bivalent metal ions. The dissociation constants (pK_1 and pK_2) of the reagent and the formation constants ($\log K_1$ and $\log K_2$) of its metal chelates have been determined potentiometrically following the Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti[1].

Experimental

The ligand 2-hydroxy-1-naphthalidene-sulphamethoxazole was prepared by refluxing equimolar quantities of 2-hydroxy-1-naphthaldehyde and the amine in alcohol-DMF mixture and was repeatedly crystallised to get an analytically pure compound, m.p 240° (observed). All the metal perchlorates used were prepared from metal salts and perchloric acid both of A. R. grade. These were standardised complexometrically by EDTA titrations[2]. Other experimental details were the same as in our earlier communication[3].

Results and Discussion

It may be mentioned here that the ligand does not undergo hydrolysis under the experimental

conditions described. This was indicated by rapid attainment of equilibrium during the course of titration and by the absence of any significant drift in pH even after two hours. This was further confirmed by taking tlc of a sample titration mixture from time to time.

In the ligand, it is the phenolic OH group that takes part in complex formation and the proton is replaced from it by the metal ion during chelation. As only one proton per ligand molecule is liberated, 'Y' the number of dissociable protons attached to each ligand molecule is one.

From the titration curves (Fig. 1), $\bar{n}_A$ values at various B values (pH meter readings) were calculated and the formation curve (B vs $\bar{n}_A$) was plotted. The pK_1^H corresponding to phenolic H was obtained by half integral method at $\bar{n}_A$=0.5. This was further corroborated by plotting the graph of log ($\bar{n}_A$/1-$\bar{n}_A$) vs B.

Volume of NaOH in ml
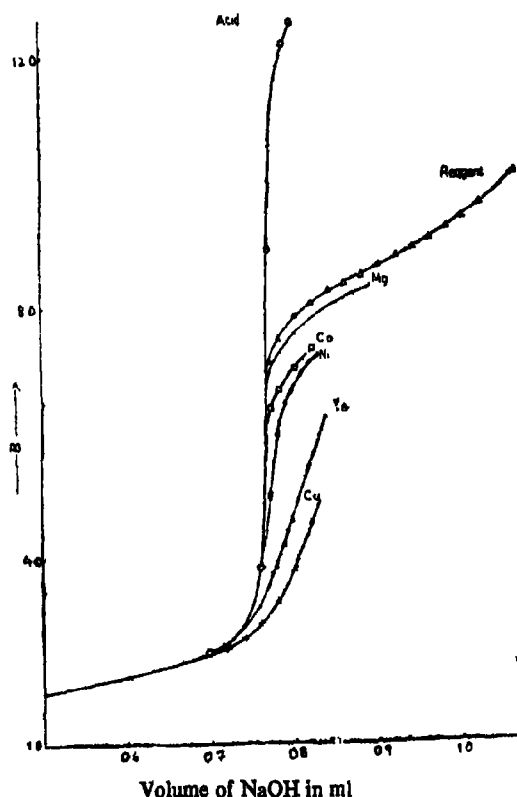
Fig. 1. Titration curves of 2-hydroxy-1-naphthalidene-sulphamethoxazole.

From the titration curves, $\bar{n}$ and pL values for metal-ligand systems were also determined. Values of log K_1 and log K_2 were determined from the curves $\bar{n}$ vs pL by half integral method and the results were corroborated by plotting the graph of $\left[\log \frac{\bar{n}}{1-\bar{n}}\right]$ vs pL. As in the cases of Cu^{2+}, Zn^{2+} and Mg^{2+} complexes the difference between log K_1 and log K_2 was found to be less than 1.78 log units, these were computed by the least square method, and the results are reported in Table 1.

Table 1—Stepwise Stability Constants of Various Complexes*

t = 25° μ = 0.1

Cations	H^+	Cu^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Mg^{2+}
log K_1	8.18	7.56	6.58	4.18	3.90	2.94
log K_2	–	6.03	5.50	–	–	2.87

* The order of stability of metal chelates is found to be $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mg^{2+}$. This is in agreement with that of Irving and Williams[4].

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The authors record their sincere thanks to Dr. D. G. Vartak, B. A. R. C., Bombay for valuable suggestions.

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Electrode Kinetics of the Polarographic Reduction of Ni(II) in the Presence of Increasing Concentrations of L-4-Hydroxyproline and L-Tryptophan

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THOUGH a few polarographic data[1,2] on the electroreduction of Ni(II) in the presence of tryptophan are mentioned in literature, systematic and comprehensive studies on the electrode kinetics of this system are laking. Besides, studies on the electrode kinetics of Ni(II) in the presence of L-4-hydroxyproline (LHP) have not been reported so far. The present paper aims at studying the influence of increasing concentrations of LHP and L-tryptophan on the kinetics of electrode reaction of Ni(II) under different conditions of pH.

Experimental

Solutions of $Ni(NO_3)_2.6H_2O$ and $NaClO_4$ were prepared from reagent grade (A. R., B. D. H.) chemicals in conductivity water. L-4-Hydroxyproline (LHP) was a Fluka (Puriss, CHR) product, and L-tryptophan was a Reanal (Hungary) A. R. product and their aqueous solutions were used. The concentration of the depolarizer was kept at $1\times10^{-3}M$ in each case and that of supporting electrolyte ($NaClO_4$) at 0.1 M. Requisite amount of Triton X-100 was added to suppress the maximum.

Polarograms of the solutions were taken at 25± 0.1° by a manual set up (Toshniwal polarograph, Model CLO2 in conjunction with a Toshniwal polyflex galvanometer, Model PL 50). Purified nitrogen gas was passed through the solutions to remove the dissolved oxygen. Saturated calomel electrode (S.C.E.) was used as a reference electrode. The number of electrons, n, involved in the reduction process was determined by millicoulometric method of DeVries and Kroon[3]. This gave the value of n equal to 2 in each case. Having known the value of n, the Ilkovic equation was used to calculate the value of D at different concentrations of LHP and L-tryptophan. The potential-dependent rate constant, $k_{f,h}$, was calculated by Koutecky's method[4]. The kinetic parameters, αn_a and $k^0_{f,h}$, were calculated from the plots of log $k_{f,h}$ vs $E_{d.e.}$. Throughout the measurements the current at the end of the drop (i.e. the maximum current) was recorded for the reasons given by Meites[5].

The d.m.e. had the following capillary characteristics (in 0.1 M $NaClO_4$, open circuit): (i) for Ni(II)-LHP system : m=2.46 mg/sec ; t=2.44 sec ; $m^{2/3}t^{1/6}$=2.11 $mg^{2/3} sec^{-1/2}$; h_{corr}=61.8 cm ; (ii) for Ni(II)-L-tryptophan system ; m=1.67 mg/sec ; t=4.04 sec ; $m^{2/3}t^{1/6}$=1.78 $mg^{2/3} sec^{-1/2}$; h_{corr}=63.0 cm.

Results and Discussion

(i) *Ni(II)-L-hydroxyproline (LHP) system* :

(a) *At constant* p*H 4* ; Ni(II) gives a single well-defined diffusion-controlled wave in the absence of LHP. With the addition of $2\times10^{-3}M$ LHP a second small wave appears at a more negative potential (−1.1 V vs S.C.E.) whose half-wave potential is −1.22 V (S.C.E.). On further increasing the concentration ($6\times10^{-3}M-4\times10^{-2}M$) the $E_{1/2}$ of the second wave remains the same but at [LHP]> $6\times10^{-2}M$, the $E_{1/2}$ becomes −1.27 V (S.C.E.). The wave-heights of both the waves are diffusion-controlled as revealed by the linearity of i_d vs $h^{1/2}_{corr}$ plots which pass through the origin. Analysis of these waves by log plots shows that both are irreversible. The more positive (first) wave may be attributed to aquo nickel ion and the second one to some complex species of nickel ion with LHP. This view is supported by the work of Pleticha[6] who obtained two waves for Ni(II) in the presence of histidine, D-arginine and methionine ; the more positive wave was attributed by him to uncomplexed nickel. As pointed out above, at higher concentrations (> $6\times10^{-2}M$) of LHP the second wave is shifted to more negative potentials. A likely explanation of this may be that upto a certain concentration of LHP ($4\times10^{-2}M$) only one form of Ni(II)-LHP complex is present as a result of interaction between LHP and Ni(II), but at higher concentrations (> $6\times10^{-2}M$) of LHP, a second species of complex is formed due to availability of excess ligand.

(b) *At constant* p*H 8* : In the absence of LHP, a single well-defined diffusion-controlled wave of aquo nickel ion is obtained. However, in the presence of $1\times10^{-2}M$ LHP two well-defined waves appear which are diffusion-controlled and irreversible. $E_{1/2}$ of the first wave corresponds to the aquo nickel ion and that of the second more negative wave ($E_{1/2}$=−1.22 V vs S.C.E.) corresponds to some complex species of Ni(II) with LHP. On further increasing the concentration of LHP ($2\times10^{-2}-8\times10^{-2}M$) the height of the first wave decreases while that of the second one increases thereby suggesting the participation of more and more nickel ion in the complex formation due to excess availability of the ligand. At still higher concentration of LHP ($10\times10^{-2}M$), the first wave disappears and only the more negative second wave persists whose $E_{1/2}$ is now shifted to more negative potential (−1.27 V vs S.C.E.). On increasing the concentration of LHP beyond $10\times10^{-2}M$, the $E_{1/2}$ of this wave records a negative shift. The fact that $E_{1/2}$ of the second wave changes from −1.22 V (upto $8\times10^{-2}M$ LHP) to −1.27 V (at $10\times10^{-2}M$ LHP) and then to ≈ 1.37 V (at LHP concentration > $4\times10^{-1}M$) clearly shows the existence of consecutively formed complex species of Ni(II) with LHP.

(c) *Influence of increasing concentrations of LHP on the kinetics of irreversible electrode reaction of Ni(II)*: On applying various tests of irreversibility[7-10] it has been ascertained that the well-established irreversible electrode reaction of Ni(II) remains the same at pH 4 and 8. As the wave-heights of the second wave at constant pH 4 are comparatively very small, an analysis of kinetic parameters for this wave to a greater degree of precision is not possible. Likewise, the analysis of kinetic data in respect of the first wave at constant pH 8 has not been taken up. Only the kinetic parameters at concentrations of LHP > $10\times10^{-2}M$, where single wave appears, have been calculated at this pH.

At constant pH 4, αn_a increases at lower concentrations (< $6\times10^{-2}M$) of LHP while at higher concentrations (> $10\times10^{-2}M$) it decreases. This shows that[11-13] the irreversible electrode reaction of Ni(II) becomes less irreversible at lower concentrations of LHP while it tends to become more irreversible at higher concentrations. An increase in the value of rate constant, $k^0_{f,h}$ at lower concentrations of LHP and a decrease in its value at higher concentrations support the above conclusions. At constant pH 8, αn_a and $k^0_{f,h}$ decrease with increasing concentrations of LHP thereby showing that the irreversible electrode reaction of Ni(II) tends to become more irreversible in the presence of increasing concentrations of LHP.

(ii) *Ni(II)-L-tryptophan system* : Ni(II) yields a single well-defined diffusion-controlled and irreversible wave in the presence of increasing amounts of L-tryptophan under different conditions of pH, viz., constant pH 4 and 7. At constant pH 7, a sharp maximum appeared on the plateau of C-V curves which, however, disappeared on the addition of 0.002% Triton X-100.

On applying various tests of irreversibility, it has been ascertained that the well-established irrever-

sible electrode reaction of Ni(II) remains the same under both the two conditions of pH. Under the two conditions of pH the rate constant, $k^{o}_{f,h}$ decreases with increasing concentrations of tryptophan. It follows from this that the irreversible electrode reaction of Ni(II) is rendered increasingly more irreversible as the concentration of tryptophan is increased. The parameter αn_a also decreases with increasing concentrations of tryptophan under different conditions of pH. The polarographic reduction of Ni(II) is a well-established 2-electron reduction process and therefore n_a, the number of electrons involved in the rate determining step, can either be 1 or 2. Since the decrease in αn_a values is indiscrete and at no stage the two consecutive values differ by a factor of 2, the possibility of a decrease in the value of the product αn_a due to a change in n_a may be ruled out. Thus it can be safely concluded that it is α which is decreasing. α, the transfer coefficient, signifies[13] the fraction of the applied voltage which favours the cathodic reaction, $Ni^{2+} + 2e \rightarrow Ni$. A decrease in the value of α thus implies that the transfer of electron/electrons is made increasingly difficult. In other words, the electrode reaction of Ni(II) is rendered increasingly more irreversible as the concentration of L-tryptophan is increased. Thus, the variations in the values of both the kinetic parameters point to the same conclusion.

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Reactivity of Indian Rock Phosphates in Presence of Oxidative Degradation Products of Coal

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THE oxidative degradation products of coal, obtained by the action of potassium permanganate in presence of rock phosphate in aqueous solution, increase the reactivity of rock phosphates resulting in the dissolution of more phosphatic content in water.

A variety of oxidizing agents, mostly in acidic medium, were used in the past for controlled low temperature degradation of coal[1]. Later, oxidation of coal in alkaline medium using potassium permanganate was studied in detail[2-6]. The different parameters upon which the oxidative degradation of coal in alkaline medium is dependent was investigated very recently by Banerji[7]. Contradictory reports [8,9] on the reactivity of Indian rock phosphates posed a great problem of its utility to chemists all over the world. The work of Johnston[10] on the dissolution of insoluble phosphate in aqueous solutions of organic acids prompted the author to design the present investigation for determining the extent of reactivity by water soluble organic acids produced in the oxidative degradation of coal by potassium permanganate in presence of rock phosphates.

Experimental

Rock phosphates from Rajasthan, Uttar Pradesh and Bihar, obtained through Geological Survey of India, were powdered, sieved (100 mesh, B.S.S.) and analysed according to the procedure of Washington[11].

A number of stoppered conical flasks were taken and 1g finely powdered sample of each rock phosphate, 0.5 g coal (dmf, 36 mesh BSS, C=80%) and 100 ml 0.1 N $KMnO_4$ solution were added in each of the flasks. The flasks with their contents were kept agitated in a mechanical shaker at room temperature (27°). After definite intervals of time the solution of each flask was allowed to stand for some time, filtered and washed with water through a sintered glass crucible. Aliquot portions were utilized for determining P_2O_5 and for measuring the extent of oxidative degradation[12]. A blank (mineral + water) estimation was also simultaneously carried out.

Phosphate was estimated volumetrically after precipitating with ammonium molybdate solution.

In order to measure the extent of oxidative degradation, a suitable portion of the aliquot was treated with solid KI and acidified with conc. HCl. The liberated iodine was titrated against a standard thiosulphate solution using starch as an indicator. Permanganate consumed by coal in different time intervals was calculated from the titre values.

Results and Discussion

The analysis (Table 1) shows that the rock phosphates contain varying amounts of P_2O_5 (12 to 30%), magnesium and iron, suitable for healthy plant growth. It is interesting to record that all the rock phosphates are alkaline in aqueous solutions.

The experimental results (Tables 2 and 3) show that the release of phosphate from rock phosphates by water is not much. However, with water soluble aromatic polycarboxylic acids, produced as a result of degradation of coal by oxidizing action of alkaline

TABLE 1—COMPOSITION OF VARIOUS ROCK PHOSPHATES

Ingredients %	RP	MNP	MPS	MGP	MVLP	MRP	I(B)RP
Insoluble material	5.60	7.56	26 05	5.90	17.26	3 24	24.14
Al_2O_3	1.42	23 05	23 92	25 51	33 90	31 26	18.96
Fe_2O_3	0.28	0.25	0 24	0 25	0.32	0 96	12.17
CaO	44.98	32.15	17.00	16 45	15.50	11.38	9 81
MgO	0.08	0 09	0.06	0 05	0.05	0.04	0 35
P_2O_5	27.18	15 46	10.34	30.17	11 97	30.72	15.60

RP - Rajasthan Phosphate,
MNP - Mussorie Nodular Phosphorite,
MPS - Mussoric Phosphorite Shale,
MGP - Mussorie Granular Phosphorite,
MRP - Mussorie Rock Phosphate,
I(B)RP - Itagarh (Bihar) Rock Phosphate.

TABLE 2—RELEASE OF P_2O_5 (G/L) FROM ROCK PHOSPHATES IN WATER AFTER 24 HR AT 27°

Period	RP	MNP	MPS	MGP	MVLP	MRP	I(B)RP
After 24 hr	0.0052	0.0045	0.0012	0.0040	0.0009	0.0033	0.0025

TABLE 3—RELEASE OF P_2O_5 (G/L) FROM ROCK PHOSPHATES IN THE OXIDATIVE DEGRADATION OF COAL AT 27°

Period	RP	MNP	MPS	MGP	MVLP	MRP	I(B)RP
After 2 hr	0.0110	0.0076	0.0023	0.0071	0.0017	0.0063	0.0048
After 4 hr	0.0137	0.0099	0.0035	0.0090	0.0030	0.0077	0.0060
After 6 hr	0 0163	0.0115	0.0047	0.0105	0.0043	0.0091	0.0077
After 8 hr	0.0223	0 0158	0.0083	0.0145	0 0075	0.0128	0.0115

permanganate in aqueous solution, the release increases to a marked extent. The colour of permanganate changes gradually from brown to colourless at the end of 8 hr showing thereby that the reduction occurs in a step wise process.

$$KMn^{7+}O_4 \rightarrow K_2Mn^{6+}O_4 \rightarrow Mn^{4+}O_2$$

According to Banerjee[7], for a typical low rank coal (C=79.2%), the optimum volume and concentration of permanganate solution for complete oxidation, i.e. when no coal particle is left over as residue, are 20.2×10^{-2} mole/litre and 225 ml/g of coal (dmf), respectively. The release of P_2O_5 from various rock phosphates shows a progressive increase with lapse of time. This is because of the fact that degradation of coal, which continues upto above 8 hr, produces more and more water soluble organic acids which help in the dissolution of increasing amount of phosphatic content.

During the course of this investigation it was noticed that after a few hours the solutions in all the systems became colloidal. This is because of the formation of finely divided hydrated manganese oxide as a result of the reduction of permanganate and intermediate formation of humic acid on account of degradation of coal. With lapse of time, further degradation of humic acid into benzene carboxylic acids occurs and the solution becomes clear.

Thus, the reactivity of Indian rock phosphates increases to an appreciable extent by the permanganate oxidation of coal.

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Triazolo [3, 4-*b*] [1, 3, 4] thiadiazoles

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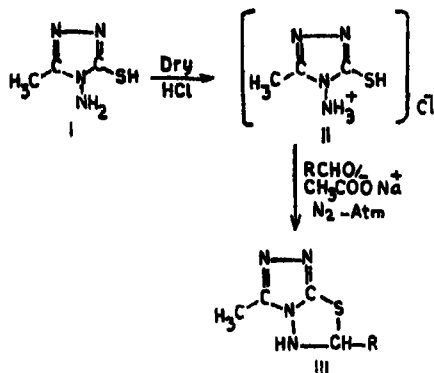
LITERATURE records[1-3] the synthesis of some *s*-triazolo [3, 4-*b*] [1, 3, 4] thiadiazoles. One such synthesis is by George *et al*[4] but the yields recorded are low. We report here the synthesis of some new *s*-triazolo [3, 4-*b*] [1, 3, 4] thiadiazoles by the modification of the above procedure, where very good yields of the compounds were obtained.

The compounds have been prepared by the condensation of 4-amino-5-mercapto-3-methyl-*s*-triazole (I) with various aldehydes in the presence of sodium acetate. The structure (III) for these compounds finds support from analysis and pmr data. PMR* of IIIa in $CDCl_3$-DMSO-d_6 showed a doublet (3*H*) at 2.37 assignable to three methyl protons at position 6. It also showed a singlet (3*H*) at 3.20 assignable to three protons of methyl group at position 3. The signals due to one proton attached to C_6 and one proton attached to nitrogen overlapped and gave a broad signal at 5.20.

*Chemical shifts in δ (ppm).

Structure III finds further support from its insolubility in dil. NaOH solution.

a, R = CH_3 –
b, R = C_6H_5 –
c, R = $C_6H_4NO_2$ – (3′)
d, R = $CH_2O_2C_6H_3$ – (3′,4′)
e, R = $CH_2O_2C_6H_2.NH_2$ – (3′,4′,6′)

Experimental

Melting points were taken in open glass capillaries in liquid paraffin bath and are uncorrected. PMR spectra were recorded on Varian 360 60 MHz spectrometer. Purity of the compounds was checked by tlc on silica gel.

4-Amino-5-mercapto-3-methyl-s-triazole (I) : It was prepared starting from thio-carbohydrazide[5] and excess of acetic acid according to the procedure described by Saikachi and Kanaoka[6].

3,6-Dimethyl-5,6-dihydro-s-triazolo [3,4-b] [*1,3,4*] *thiadiazole :* A slow stream of dry hydrochloric acid gas was passed through a chilled ethereal suspension (20 ml) of 4-amino-5-mercapto-3-methyl-*s*-triazole (1. 3 g ; 0.01 mole) till it was saturated. Ether was decanted off completely and the residue was suspended in absolute ethanol (40 ml). To this, fused sodium acetate (0.90 g ; 0.011 mole) and freshly distilled acetaldehyde (2 2 g ; 0 05 mole) were added. The contents were refluxed over a steam bath under nitrogen atmosphere. The suspension started dissolving and a new solid separated out. Refluxing was continued for 4 hr when it was cooled. The separated solid was collected under suction and washed with water. Crystallisation from ethanol gave faint cream coloured long plates, m.p. 211°, yield 1.0 g (65%).

TABLE 1—METHYL-5,6-DIHYDRO-*s*-TRIAZOLO [3, 4-*b*] [1, 3, 4] THIADIAZOLES WITH SUBSTITUTIONS IN POSITION 6.

Sl. No.	R	Time taken for the reaction (hr)	m.p. °C	Yield %
a	CH_3	4	211	65
b	C_6H_5	4	203	75
c	$C_6H_4NO_2$-(3′)	8	227	60
d	$CH_2O_2C_6H_3$-(3′, 4′)	4	219	68
e	$CH_2O_2C_6H_2NH_2$-(3′, 4′, 6′)	6	300	55

All the compounds were crystallised from ethanol.
All compounds gave consistent C, H and N analysis.

Similarly, other aldehydes, namely benzaldehyde, *m*-nitrobenzaldehyde, piperonal and *o*-amino piperonal were condensed with 4-amino-5-mercapto-3-methyl-*s*-triazole. The yield of these products, their m. p. and time required for the reaction are tabulated in Table 1. All the compounds were crystallised from ethanol. They also gave consistent carbon, hydrogen and nitrogen analysis.

Acknowledgement

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Synthesis and Antifungal Activity of Oxazolones

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4-(2-Chlorophenylhydrazone)-3-methyl-5-isoxazolone is the only compound in the oxazolone and isoxazolone family of compounds which has been used against fungus[1]. During our work on the synthesis and activity studies of some new heterocyclic compounds, we found that 2-phenyl-4-(α-methylbenzal)-5-oxazolones are quite active against fungus. This paper describes synthesis of some oxazolones and their activity against the fungi *Alternaria solani*, *Colletotrichum capsici* and *Choanephora cucurbitarum*.

2-Phenyl-4-(α-methylbenzal)-5-oxazolones (III) have been prepared by the reaction of azlactone, prepared *in situ* by the action of acetic anhydride on hippuric acid in presence of sodium acetate, with α-methylbenzalbenzylamines. The products are obtained probably by the elimination of benzylamine from the addition products of azlactone with corresponding imines. First step in the mechanism[2,3] is the abstraction of a proton from the active methylene function of azlactone to give an enolate which undergoes electrophilic addition with the imines to yield unstable addition product (II). Subsequent

elimination of benzylamine in presence of base affords III as shown in Chart 1.

$$C_6H_5-\overset{O}{\overset{\|}{C}}-NHCH_2COOH \xrightarrow{Ac_2O} \text{(I)}$$

(I): $H_2C-C=O$ ring with N, O, $C-C_6H_5$

$$\text{I}+R-C_6H_4-\overset{CH_3}{\overset{|}{C}}=N-CH_2C_6H_5 \rightarrow R-C_6H_4-\overset{CH_3}{\overset{|}{C}}-NH-CH_2-C_6H_5$$

with $HC-C=O$, N, O, $C-C_6H_5$ ring

(II)

$$\downarrow -C_6H_5CH_2NH_2$$

$$R-C_6H_4-\overset{CH_3}{\overset{|}{C}}=C-C=O$$

with N, O, $C-C_6H_5$ ring

(III)
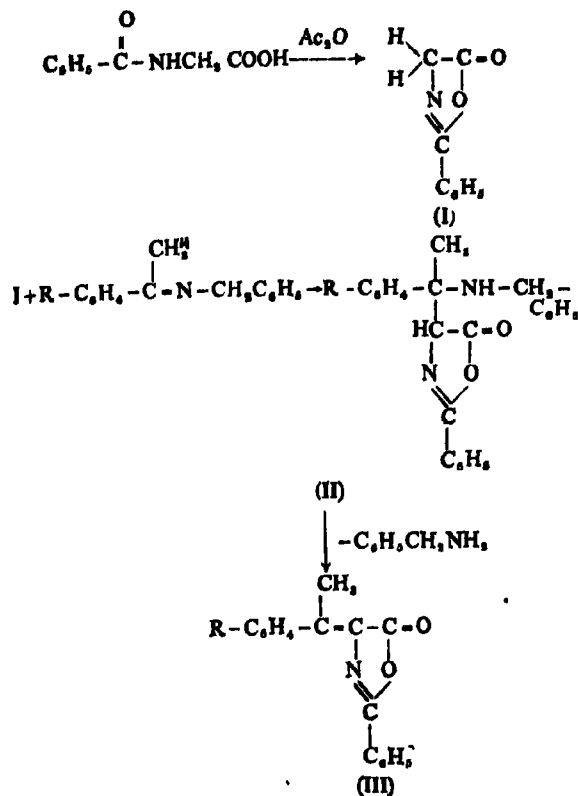
Chart 1

The oxazolone structure assigned to these products has support from elemental analysis, ir, nmr and mass spectra. IR spectrum of IIIa showed bands at 1750 and 1670 cm^{-1} indicative of carbonyl group and C=N linkage, respectively. NMR spectrum of IIIb showed three methyl protons as a singlet at 7.7 τ and nine aromatic protons as a multiplet between 2.2 to 2.8 τ. In mass spectra, molecular ion peaks constituted the base peaks. Mass and nmr spectra further indicated that acylation of OH and NH_2 groups also took place under the reaction conditions.

The products (Table 1) are found to be identical (m.m p.) with the authentic samples of the respective oxazolones synthesized by an unambiguous route[4].

TABLE 1—2-PHENYL-4-(α-METHYLBENZAL)-5-OXAZOLONES (III)

Compound	R	m p* °C	Yield %
IIIa	p-OC_2H_5	37	70
IIIb	p-Cl	250	80
IIIc	p-$OCOCH_3$	100	75
IIId	m-NO_2	70	80
IIIe	p-CH_3	167	80
IIIf	p-$NHCOCH_3$	143	75
IIIg	o,p-Br_2	138	70
IIIh	o,p-$(OCOCH_3)_2$	153	70

*All melting points are uncorrected.
All the compounds gave satisfactory elemental analysis.

The above oxazolones (IIIa-IIIh) along with 2-phenyl-4-(α-methylbenzal)-5-oxazolone (IIIi) and 2-phenyl-4-(α-methyl-p-bromobenzal)-5-oxazolone (IIIj) were tested for their antifungal activity against *Alternaria solani, Colletotrichum capsici* and *Choanephora cucurbitarum* by poisoned food technique. For each compound three concentrations viz. 1000, 500 and 250 ppm were tried. Compounds IIIb, IIId, IIIf, IIIg and IIIh completely inhibited all the three fungi at 1000 ppm. The other five compounds were not so effective even at 1000 ppm. A detailed study of the structure activity relationship showed that the presence of Cl, NO_2 and $NHCOCH_3$ groups in phenyl ring of oxazolone increased the activity of unsubstituted oxazolone IIIi. Another interesting feature of the study was that while the presence of one Br or $OCOCH_3$ in the phenyl ring had little effect on the activity, presence of two Br or two $OCOCH_3$ in the phenyl ring (IIIg and IIIh) made these oxazolones the most effective.

Experimental

Reaction of azlactone with α-methyl-p-chlorobenzalbenzylamine: Hippuric acid (1.8 g) and α-methyl-p-chlorobenzalbenzylamine (0.01 mole) were dissolved in dry benzene (50 ml). Acetic anhydride (1.2 ml) and sodium acetate (0.5 g) were added to the solution. The mixture was just heated to get a clear solution and left at room temperature for 2 days. During this period most of the product precipitated which was filtered off. The mother liquor on concentration gave more of the product. The product was recrystallized from hot benzene, m.p. 250° (yield 80%). Other oxazolones were synthesized in similar manner.

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Amoebicidal Testing of Drugs—Use of Goat Serum as a Substitute for Horse Serum for Growing *Entamoeba histolytica*

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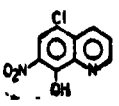
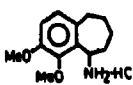
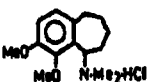
AMOEBIASIS is one of the most prevalent diseases in tropical countries like India. Unfortunately, even today, the disease is not diagnosed adequately and critically though prolonged amoebiasis causes ulcerations, hepatic complications, liver

abscess and other associated diseases. It is, however, well established that an ideal antiamoebic agent should be capable of eradicating the causative organism *Entoamoeba histolytica* both from the bowel and from extra intestinal sites at non-toxic doses[2,3]. Though a number of useful drugs have been synthesised, they are not found to be universally effective or ideal and are usually associated with side effects. Moreover, need for drugs with sustained prophylatic actions are widely felt[1]. But no single preparation satisfy all these requirements.

In our attempt to study the synthesis of new antiamoebic drugs based on the physico-chemical properties of different known antiamoebic drugs and their biological properties, it has been found necessary to screen the different antiamoebic agents in the laboratory by proper *in vitro* testing.

E. histolytica is generally grown in Boeck and Drbohlav medium consisting of egg slant of horse serum overlay with bacteria plus rice starch. In view of high cost of horse serum and the difficulty in obtaining its regular supply, Dutta[8] used bovine serum as a substitute for growing *E. histolytica.* However, availability of goat serum is comparatively easy in Kalyani and we prefer to use goat serum as a substitute for horse serum.

We report in this communication our attempt to use goat serum as a substitute for horse serum or bovine serum for growing *E. histolytica*, and to standardize and test the method by using some known antiamoebicides and screen a few unknown compounds. Study of amoebicidal properties of drugs in different media would be helpful in comparing amoebicidal action of antiamoebic drugs against axenically grown *E. histolytica* and in different medium using horse, bovine or goat serum

Experimental

Preparation of serum : For the preparation of serum and screening of drugs, we followed the same procedure as reported by Dutta *et al*[8,9]. Fresh goat blood was collected from Kalyani market in a thermoflask. The serum was decanted, centrifuged at 2000 rpm for about half an hour and filtered through sintered glass filter. The filtered serum was taken in a clean dry sterilised conical flask, inactivated in a thermostat at 56° for about 1 hr and stored at 4°. The stored serum was diluted eight fold with 0.85% normal saline in $M/40$ phosphate buffer (pH=7.0) before use.

Technique of cultivation : A series of test tubes and Erlenmeyer flasks were thoroughly cleaned, dried, plugged with cotton and sterilised at 150° for 1 hr in an air-oven. 8 eggs (Hen) were thoroughly cleansed with detergent and subsequently sterilized with alcohol. The eggs were broken and the contents emulsified with $M/40$ phosphate buffer and filtered through a sintered glass filter. Different strains of *E. histolytica* were grown in the flasks with diluted goat serum, mixed bacterial flora and rice starch at 37°. Sub-cultures were made every 48 hr. 5 ml of emulsified egg solution was poured in each of the sterilised test tubes placed at an angle of 45° and heated at 80° for 1 hr in an air-oven. The heating was repeated thrice in succession. The appearance of turbidity in the contents of the medium indicated lack of proper sterilization and caused immediate rejection. *E. histolytica* was cultured in these test tubes. 0.2% solutions of acriflavin and gentian violet were used to prevent overgrowth of fungal and bacterial flora.

Isolation of strain of E. histolytica : LD strain of *E. histolytica* was isolated from fresh stool samples collected from Usha 'X'-ray clinic, P. O. Ranaghat, Nadia. Both trophozite and cystic forms of *E. histolytica* were present. The sample was washed with 0.85% NaCl solution and transferred into goat serum medium. This was repeated several times and the contents were examined under the microscope (10X-90X). Trophozite form of *E. histolytica* was collected in this way and preserved. Strain collected from the School of Tropical Medicine, Calcutta, was also used.

TABLE 1—*In vitro* ACTIVITIES OF AMOEBICIDAL DRUGS

Drugs	Amoebicidal concentration (µg/ml) 48 hr
Enteroquinol	62.5
Enteroviaform	62.5
Diiodoquinol	500.00
Chloroquine-phosphate	500.00
Metronidazole	7.81
5-Chloro-7-nitro-8-hydroxy quinoline+	15 6
Emetine hydrochloride	7.81
Glycobiarsol	500.00
Furanidazole	62 5
Clephamide	62.5
6-Amino-5-spiro-(4,5)-decane/hydrochloride+	15.6
1-*n*-Butyl-3,4-dimethoxy-5-amino-5,6,7,8,9-pentahydro-benzocyclo heptene/hyrochloride+	62 5
1-*n*-Butyl-3,4-dimethoxy-5-dimethyl amino-5,6,7,8,9-pentahydro-benzocyclo heptene/hydrochloride+	250.00

+ The compounds were synthesised by Prof. B. C. Pathak *et al*, Department of Applied Chemistry, University of Calcutta. The other drugs were procured from The Central Drug Laboratory, Calcutta and from Prof. B. C. Pathak.

TABLE 2—COMPARISON OF AMOEBICIDAL ACTIVITIES (μg/ml) REPORTED BY VARIOUS WORKERS

	Philips[7]	Nakamora and Anderson[8]	Bradner and Rawson[9]	Diamond and Bartgis[10]	Dutta and Yadava[4]	Present study
Strain of *E. histolytica*	F-22	F-22	F-22	F-22	NIH 200	LD 1
Period of incubatin with drug	48 and 72 hr	48 hr	48 hr	72 hr	72 hr	48 and 72 hr
Emetine-hydrochloride	5	10	31.2	6	11.7	7.8* (3.9-7.8*)
Metronidazole	–	–	–	0.75-1.5	3.9	3.9-7.8*
Enterovioform	–	40-50	125	–	31 2	62.5
Chloroquine phosphate	–	–	–	–	1000	500
Diiodoquine	–	200	1000	–	375	500

Upper limit (3.9—7.8—activity is observed within these limits)

Examination and sub-culture of E. histolytica : Four day old cultures were examined under an inverted microscope (10X ocular and 20X objective) and the tubes showing $20-30\times10^{4}$ amoebae/ml were used as seed for sub-culturing fresh tubes. For sub-culture, 0.2 ml of this amoebic suspension was inoculated into each tube containing 8.8 ml of the medium and the cultures were incubated vertically at 37°.

Drug testing : Most of the drugs are insoluble in water. Some of the drugs are dissolved in a little DMF solution. In general, fine suspensions of drug were made by adding gum acacia. 1 ml of drug suspension in normal saline (10 mg/ml) was added to each culture tube containing 9 ml inoculated medium (8.8 ml medium+0.2 ml inoculum) in duplicate to give a drug concentration of 1000 μg/ml per tube. Each tube contained 23.75×10^{4} amoebae/ml. Successive two-fold serial dilutions (eight) of the drug in sterile normal saline was added in subsequent duplicate tubes. Strict aseptic conditions were maintained. Drug suspensions were sterilized by autoclaving at 10 1b/sq inch for 15 min at 120°. The tests were run for 72 hr (though 48 hr are sufficient) and incubation was carried out at 37°. Amoebicidal end point was examined on the basis of presence or absence of living amoebae by direct observation under a microscope and by sub-culture.

The operations were repeated to examine the reproductibility of the results. The results of some known and unknown drugs are recorded in Table 1.

In vitro activities of antiamoebic drugs against *E. histolytica* have been widely reported[4-10]. Variations of end points depending on conditions are also noted.

Discussions

The results presented in the Table 1 and Table 2 show that goat serum can be successfully utilised instead of horse serum for the culture of *E. histolytica*. The results also show that all the unknown compounds particularly spiroamino hydrochloride and 5-chloro-7-nitro-hydrooxyquinoline can be successfully used as antiamoebic drugs. Spiroamino hydrochloride and its derivatives should receive special attention as amoebicidal properties of these compounds are not yet reported.

It will be quite pertinent to compare some of results with those reported earlier (Table 2). Slight variations in results appear reasonable in view of different strains and culture media. Furthermore, insolubility of the drugs poses a big problem and variations of minimum inhibitory concentration (MIC) appear natural. We have reported the upper limits of MIC taking into consideration all these limitations.

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Phytochemical Studies on *Eclipta alba*

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ECLIPTA alba (Compositae), popularly known as 'Bringraj' is an annual herb, growing in moist environment all over India. It is reputed for its high medicinal values[1]. A perusal of literature revealed that the leaves and stems of the plant have been examined chemically[2-7] but no phytochemical study of the roots of this plant seems to have been done. A systematic study of this part was therefore undertaken and the results are reported here.

The dried and crushed roots (2 Kg) were extracted exhaustively with hot petroleum ether (60-80°) and ethanol successively. The concentrated petroleum ether extract was saponified with 0.5 *N* KOH. It yielded an unsaponifiable matter which was extracted with ether. The aqueous layer had some insoluble floating material which was separated and dissolved in chloroform. Chloroform was distilled off under reduced pressure to give a cream coloured solid which on column chromatography over silica gel afforded compound (A) and (B). The concentrated ether extract was chromatographed with petroleum ether : ether (1 : 4) to give compound (C). After refluxing with benzene the concentrated ethanolic extract of the root was chromatographed over silica gel to give compound (D).

Compound (A) : Elution with petroleum ether : benzene (1 : 1) yielded a white compound, m.p 86-87°, $C_{31}H_{64}O$; ir ν_{max}^{KBr} cm^{-1} 3289, 775 and 772, mass spectrum, m/e 434 [M^+-H_2O], 406 [M^+-H_2O-C_2H_4] and 31 (-CH_2OH).

It was characterised as hentricontanol[9] by co-tlc and m.m.p. with an authentic sample and by preparing its acetate, m.p. 69-70°, iodide, m.p. 69° and hentricontanoic acid, m.p. 98°.

Compound (B) : Elution with ethanol : benzene (1 : 1) afforded a white solid compound, m.p. 78-79°, $C_{27}H_{56}O$, ir ν_{max}^{KBr} cm^{-1} 3440, 1100, 765 and 720. It formed an acetate, m.p. 44-45°. It was identified as heptacosanol-14 by co-tlc and m.m.p. with an authentic sample.

Compound (C) : Elution with petroleum ether : ether (1 : 4) gave colourless needles, m.p. 166-68°, $C_{29}H_{48}O$, [M^+ 412], $[\alpha]_D$-46° ; ir ν_{max}^{KBr} cm^{-1} 3510, 1650, 995, 845 and 800. It responded to all the tests for a sterol. It formed an acetate, m.p. 141-43° and benzoate m.p. 158-60°. The identity of this compound with stigmasterol was established by m.m.p. and co-tlc with an authentic sample.

Compound (D) : Elution of the column with petroleum ether : benzene (1 : 3) afforded a white crystalline compound, m.p. 196-98°, $C_{30}H_{50}O$, [M^+ 426], $[\alpha]_D$+84°. It gave LB tests and Nollers reaction for triterpenoids. IR ν_{max}^{KBr} cm^{-1} 3200, 1653, 1470, 1000 and 828 ; acetate, m.p. 237-39° and benzoate, m.p. 233-35°. The identity of the compound was established by m.m.p. and co-tlc with an authentic sample.

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Use of Potassium Bromate : Oxidation of Aldehydes

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BENZALDEHYDE was oxidised to benzoic acid with potassium bromate under acidic condition in this laboratory[1]. The establised optimum condition has been utilised for the oxidation of *o*-, *m*-, *p*-nitrobenzaldehydes, *o*-, *m*-, *p*-chlorobenzaldehydes, *o*-, *m*- and *p*-methoxybenzaldehydes to furnish the corresponding substituted benzoic acids in almost quantitative yield. Only *o*- and *m*-methoxybenzoic acids were found to undergo bromination to some extent during oxidation in acetic acid. This

difficulty has been overcome by using acetone as the bromine scavenger. But salicylaldehyde and vanillin could not be oxidised to the corresponding acids under similar experimental condition showing that phenolic aldehydes are unsuitable for bromate oxidation. Cinnamaldehyde produced cinnamic acid in moderate yield indicating that the double bond remained unaffected by bromate. Citral, on the other hand, failed to produce the desired acid and butyraldehyde furnished impure butyric acid. Bromine was evolved in each case. It appeared that aliphatic aldehydes were difficult to oxidise. It was also observed that the use of dilute sulphuric acid during the bromate oxidation of substituted benzaldehydes holding ring-activators favoured the introduction of bromine atom in the ring in a regioselective manner, the electron attracting groups accelerated the rate of oxidation while the electron releasing groups retarded it. From the kinetic study[2] carried out in dilute acetic acid solution, it has been found that the rate of oxidation of the aldehyde at temperature ranging from 40 to 60° is dependent on the substrate and acetic acid but not on the oxidant. The oxidation of other classes of organic compounds is under investigation.

Experimental[1]

General procedure: A mixture of weighed amount of substituted benzaldehyde and half its weight of potassium bromate in acetic acid (15 ml per g of starting aldehyde) was heated under reflux for 15 min. Bromine evolved which escaped the reaction mixture. The latter was cooled, poured onto water, saturated with sodium chloride and extracted thrice with chloroform. The organic layer was extracted with saturated sodium bicarbonate solution, washed with water and dried over anhydrous sodium sulphate. On removal of the solvent no starting material was obtained excepting cinnamaldehyde, salicylaldehyde and citral. The alkaline extract was acidified with dilute sulphuric acid (congo red) and the precipitated organic acid was extracted thoroughly with either chloroform or ether. The organic layer was washed with small amount of water, dried and the solvent removed to furnish the desired acids which were crystallised, if required, for further purification. The results are presented in the order: derived acid (% yield), melting point[ref], spectral data and/or other supporting evidence and [Remarks if any]. The ir spectra were taken in Perkin-Elmer Model 597 Infrared grating spectrophotometer. The m.m.p. of each solid product with authentic specimen remained undepressed. (a) 2-Nitrobenzoic acid (95%), 142° [3a]. (b) 3-Nitrobenzoic acid (99%), 136° [3a], N.E. 165±5 [no bromination during oxidation if 4 *N* sulphuric acid is used]. (c) 4-Nitrobenzoic acid (99%), 241° [3b]. (d) 2-Chlorobenzoic acid (90%), 137° [3c]. (e) 3-Chlorobenzoic acid (85%), 157° [3d], N.E. 152±5. (f) 4-Chlorobenzoic acid (90%), 237° [3d]. (g) 2-Methoxybenzoic acid (72%), 101° [3e], ν_{max}^{KBr} 1690, 1610, 1590, 1470, 1430, 1310, 1295, 1230, 1045, 935, 910, 805 and 760 cm^{-1}; N.E. 150±5, [5 ml of acetone was used per g of 2-methoxybenzaldehyde during oxidation, otherwise brominated product, m.p. 120-135° was obtained]. (h) 3-Methoxybenzoic acid (55%), 105-107° [3e], ν_{max}^{Nujol} 1693, 1607, 1586, 1462, 1379, 1310, 1291, 1230, 1121, 1105, 1069, 1043, 936, 908, 891, 869, 810, 755, 679 and 665 cm^{-1}; [acetone was used during oxidation as in (g)]. (i) 4-Methoxybenzoic acid (90%), 182° [3f], ν_{max}^{KBr} 1680, 1605, 1580, 1515, 1425, 1305, 1260, 1180, 1170, 1132, 1108, 1025, 925, 895, 825, 775, 698, 635, 615, 605 and 540 cm^{-1}; N.E. 151±5, [mineral acid induced bromination during oxidation]. (j) Cinnamic acid (40%), 131° [3g] [recovered cinnamaldehyde, 55%, b.p. 210-220°]. (k) Butyric acid (55%), b.p. 130-140°/water aspirator [contained traces of bromo-compound].

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Potentiometric Determination of Niobium(V) in Presence of Tantalum in Non-Aqueous Media[1]

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NIOBIUM salts hydrolyse easily in aqueous media and their direct estimation in such media presents some difficulty. Many niobium compounds are soluble in non-aqueous media but their estimation by usual methods takes time. Estimation of niobium or tantalum in the presence of each other is also considered difficult.

Bismuth has been estimated using 5-mercapto-3-phenyl-1,2-thio-1,3,4-thio-diazolone-2-phenyldithio-diazolone (MPTTPT) in acid medium when a reddish-coloured precipitate is obtained Bismuth has also been detected and estimated colorimetrically using this reagent. The reagent also forms yellow precipitates with gold, mercury, lead, silver, platinum, arsenic and antimony; white with cadmium, zinc; brown with copper; brick red with tin and red with palladium[1,2].

The authors earlier reported the gravimetric estimation of niobium using the reagent in aqueous media[3]. No reference has been found in literature regarding the use of this reagent in electrometric methods.

Experimental

E.M.F. measurements were made with a digital pH meter (ECL Model PH 5651) having a single glass-calomel electrode assembly.

Preparation of niobium solution : Requisite quantity of niobium pentachloride (Fluka) was dissolved in absolute alcohol. Care was taken to avoid moisture while weighing.

Preparation of the reagent : The reagent was prepared by the described method[4]. The compound is fine white needles, m. p. 259° and is soluble in water and warm alcohol.

MPTTPT was dissolved in slightly warm absolute alcohol. The strength of the reagent solution was kept the same as that of the niobium pentachloride solution.

5 ml of niobium pentachloride solution was taken in the cell every time and the titrant (MPTTPT reagent) solution added from a microburette. Direct and reverse titrations were performed. Several such experiments were performed using 0.01M, 0.005M and 0·004M solutions of niobium pentachloride. In all the titrations, sharp change was noticed at the equivalence point after which the potential became steady again. The end-point was obtained from the maximum of $\triangle E/\triangle V$ and corresponds to 1 : 1 complex.

It is noteworthy that tantalum does not interfere in the estimation of niobium by this method. The method described above is rapid and accurate for the estimation of such compounds of niobium which get hydrolysed in aqueous media but are soluble in absolute alcohol.

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Determination of Equilibrium Constant of Ferric Formato Complex by Paper Electrophoresis

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PAPER electrophoresis has been applied to the study of metal complexes in solution. Attempts have also been made to determine the stability constants of the complex species[1-10].

As far as we are aware the stability constant has not been determined from the eluate of the cationic and anionic species of the migrant obtained after paper electrophoresis. In the present study, an attempt has been made to determine the equilibrium constant of the Fe(III)-formate system by paper electrophoresis.

Experimental

Preparation of migrant solution : $FeCl_3.6H_2O$ (1.0100 g) was dissolved in 30 ml water with addition of a few drops of hydrochloric acid. The solution was filtered and the volume made up to 50 ml.

Preparation of the background electrolyte : Stock solutions of 2M formic acid, 2M sodium formate and 1M sodium nitrate were prepared. The background electrolyte consisted of a mixture containing 25 ml 2M sodium formate, 25 ml 2M formic acid and 50 ml 1M sodium nitrate per 100 ml solution. Sodium nitrate was used to attain the desired ionic strength. Formate concentration was fixed, ionic strength was 1.0 and the pH of the electrolyte was 3.75.

Instrument : Wieland and Fischer type horizontal set was used[11]. The apparatus used was the cassette type and chromatograms could be run simultaneously on six paper strips. High voltage electrophoresis was carried out for 20 min at 400 volts and at 30°. Whatman No. 1 paper strips (3 × 40 cm) were used with an applied voltage gradient of 8 volt/cm.

pH measurements were made with an Elico Model L1-10 pH meter using a glass-calomel electrode assembly.

Procedure : The midpoint of each paper strip was marked and moistened with the background electrolyte and a spot of the metal solution was applied on it. The electrophoretic migration of the metal spots of different volume on the paper was observed. After electrophoresis, the spots of Fe(III) were developed with yellow ammonium sulphide. Two species were obtained in each case, one moved towards the anode and the other towards the cathode. The distances of the leading and tailing edges of the spots from the marked centre were measured. Portions of the paper containing the ions were cutout from the dried undeveloped electrophoregram after matching the positions of the ions with a developed electrophoregram subjected to identical electrophoretic conditions and environment. The paper portions containing the ions were treated with 0.8 N H_2SO_4, to extract the ion. The extracts derived out of the strips through washings were taken in a 25 ml volumetric flask and the volume made upto the mark with 0.8 N H_2SO_4. Similarly, blank solutions were prepared. The absorbance of the eluted iron solution was measured against these blanks at 305 mμ (Table 1).

In both the anionic and cationic species the metal ion Fe(III) present in each case was calculated

using the equation,

$$C=\frac{A}{\epsilon}=\frac{\text{Absorbance}}{\text{Extinction coefficient}}$$

where C=concentration in molarity, ϵ=2180[12].

TABLE 1

Migrant $FeCl_3$	A anionic species	A cationic species
0.04 ml	0.02	0.002
	0.033	0.005
	0.021	0.002
0.08 ml	0.062	0.01
	0.064	0.01
	0.058	0.01
0.12 ml	0.210	0.017
	0.088	0.015

With these concentrations of anionic and cationic species the equilibrium constant K was calculated in each case using the equation

$K=\frac{[Fe(OOCH)_6^{3-}]}{[Fe^{3+}]\,[HCOO^-]^6}$. The equilibrium constant K and its logarithm are shown in Table 2.

TABLE 2

Migrant $FeCl_3$	K	log K	Mean log K	log K from literature (e.m.f. method)
0.04 ml	640	2.81		
	704	2.85		
	672	2.83		
0.08 ml	640	2.81	2.83	3.1
	661	2.82		
	619	2.79		
0.12 ml	790	2.90		
	625	2.80		

Discussion

In the presence of an excess of formate ion, the positive metal ion is complexed to form $[Fe(OOCH)_6]^{3-}$ when the background electrolytes used are 25 ml 2*M* HCOONa, 1-15 ml 2*M* HCOOH, 50 ml 1*M* $NaNO_3$ and 24-10 ml water at the *p*H range 5.15 to 3.97.

$$Fe^{3+}+6HCOO^- \rightleftharpoons [Fe(OOCH)_6]^{3-}$$

But when the background electrolyte used is 25 ml 2*M* HCOONa, 25 ml 2*M* HCOOH, 50 ml 1*M* $NaNO_3$ at *p*H 3.75, the positive metal ion forms both the anionic and cationic species.

Electrophoretic study reports that most of the metal ion is complexed to form $[Fe(OOCH)_6]^{3-}$ and a trace amount of metal ion moves as a simple cation. So there must exist an equilibrium

$$Fe^{3+}+6HCOO^- \rightleftharpoons [Fe(OOCH)_6]^{3-}$$

$$K=\frac{Fe(OOCH)_6^{3-}]}{[Fe^{3+}]\,[HCOO^-]^6}$$

where K is the equilibrium constant.

Conclusion: Paper electrophoresis technique is limited to charged species, and the precision of the method is not as high as that of other physicochemical methods. Nevertheless, it is of interest in the metal-ligand system in solution since complex formation is widely used in effecting separations of metal ions.

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Relative Stability of Formato Complexes by Paper Electrophoresis

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STUDIES on the relative stabilities of various inorganic compounds have been reported earlier[1-5]. While the oxalate, citrate, tartrate and malate complexes have been investigated, none of these studies relates to the relative stability of the formato complexes. It was therefore decided to study the relative stability of formato complexes of Fe(III), Cu(II), Ni(II) and Co(II) by paper electrophoresis.

Experimental

Migrants: 2% solution of $CuSO_4.5H_2O$, $FeCl_3.6H_2O$, $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ were used as migrants.

Electrolytes: Stock solutions of 2*M* sodium formate, 2*M* formic acid and 1*M* sodium nitrate were prepared. Sodium nitrate was used to attain the desired ionic strength.

Procedure : Whatman No. 1 (1 cm × 34 cm) paper strips were taken. The electrophoretic movement of a drop of migrant under the potential difference of 220 volts for 45 min in different carrier electrolytes are recorded in Tables 1 to 3.

It appears from Table 1 that Fe(III) and Cu(II) migrate towards the anode at high concentration (1*M*-0.4*M*) of Na-formate when *p*H of the carrier electrolyte is 8.9-8.7 and ionic strength is constant while Co(II) and Ni(II) ions migrate towards the cathode. It means that Fe(III) and Cu(II) ions form anionic complexes with the carrier electrolyte and Co(II) and Ni(II) do not form such complexes. But at low concentration of sodium formate as electrolyte (0 25 *M* and below), Fe(III) is precipitated at the point of application, Cu(II) moves towards the cathode i.e. Cu(II) forms cationic species with the background electrolyte while Co(II) and Ni(II) behave as before.

From the resulting data, formation of M-formate and M′-formato complex, where M = Ni(II), Co(II) and M′ = Fe(III), Cu(II) is inferred. The data shows that Fe(III)-formato complex is more stable than Cu(II)-formato complex. Therefore, the relative stability of Fe(III)-formato complex is higher than that of Cu(II)-formato complex.

TABLE 1

Carrier electrolyte	Distance migrated in cm ('+' anionic movement ; '−' cationic movement)			
	Fe(III)	Cu(II)	Ni(II)	Co(II)
(1) 50 ml 2*M* Na-formate + 50 ml water *(1*M*), *p*H = 8.9	+ 0.2 to + 0.9	+ 0.5 to + 2.1	− 0.7 to − 2.8	− 0.8 to − 2.4
(2) 25 ml 2*M* Na-formate + 25 ml water + 50 ml 1*M* $NaNO_3$ *(0.5*M*), *p*H = 8.72	+ 0.2 to + 0.5	+ 0.3 to + 2	Cationic	Cationic
(3) 20 ml 2*M* Na-formate + 20 ml water + 60 ml 1*M* $NaNO_3$ *(0.4*M*), *p*H = 8.70	0 to + 0 4	+ 1.1 to − 0.5	Cationic	Cationic
(4) 12 5 ml 2*M* Na-formate + 12 5 ml water + 75 ml 1*M* $NaNO_3$ *(0.25*M*), *p*H = 8.60	ppt at the point of application	− 1.1 to − 2.7	Cationic	Cationic
(5) 5 ml 2*M* Na-formate + 5 ml water + 90 ml 1*M* $NaNO_3$ *(0.1*M*), *p*H = 8.4	ppt at the point of application	− 1.8 to − 3.2	Cationic	Cationic

*p*H (8.9-8 4), ionic strength constant, Na-formate variable.
*Conc. of formate in the solution and *p*H.

TABLE 2

Carrier electrolyte	Distance migrated in cm ('+' anionic movement ; '−' cationic movement)			
	Fe(III)	Cu(II)	Ni(II)	Co(II)
(1) 50 ml 2M HCOONa + 50 ml 2*M* HCOOH *(1 *M*)	+ 1.9 to + 3.3	+ 2.4 to + 5.3	Cationic	Cationic
(2) 25 ml 2*M* HCOONa + 25 ml 2*M* HCOOH + 50 ml 1*M* $NaNO_3$ *(0.5*M*)	+ 1.2 to + 2.6	+ 1.2 to − 0.5	Cationic	Cationic
(3) 20 ml 2*M* HCOONa + 20 ml 2*M* HCOOH + 60 ml 1*M* $NaNO_3$ *(0.4*M*)	+ 1.1 to + 2.3	− 0.3 to − 1.9	Cationic	Cationic
(4) 12 5 ml 2*M* HCOONa + 12.5 ml 2*M* HCOOH + 75 ml 1*M* $NaNO_3$ *(0.25*M*)	+ 0.6 to + 1.9	− 1.6 to − 2.7	Cationic	Cationic
(5) 10 ml 2*M* HCOONa + 10 ml 2*M* HCOOH + 80 ml 1*M* $NaNO_3$ *(0.2*M*)	+ 0.4 to + 2	− 1.9 to − 3.2	Cationic	Cationic
(6) 5 ml 2*M* HCOONa + 5 ml 2*M* HCOOH + 90 ml 1*M* $NaNO_3$ *(0.1*M*)	− 0.1 to − 1 (having a tendency to precipitate)	− 2.4 to − 3.8	Cationic	Cationic

*p*H = constant, ionic strength = 1, formate variable.
* Concentration of formate ion in solution.

TABLE 3

Carrier electrolyte	Distance migrated in cm ('+' anionic movement; '−' cationic movement) Fe(III)	Cu(II)	Ni(II)	Co(II)
(1) 25 ml 2*M* HCOONa + 1 ml 2*M* HCOOH + 50 ml 1*M* $NaNO_3$ + 24 ml water (*p*H = 5.15)	+1.8 to +3.9	+2.4 to +5.6	Cationic	Cationic
(2) 25 ml 2*M* HCOONa + 2.5 ml 2*M* HCOOH + 50 ml 1*M* $NaNO_3$ + 22.5 ml water (*p*H = 4.75)	+0.8 to +1.9	+2.6 to +4.6	Cationic	Cationic
(3) 25 ml 2*M* HCOONa + 5 ml 2*M* HCOOH + 50 ml 1*M* $NaNO_3$ + 20 ml water (*p*H = 4.45)	+0.5 to +2.1	+2.1 to +3.7	Cationic	Cationic
(4) 25 ml 2*M* HCOONa + 10 ml 2*M* HCOOH + 50 ml 1*M* $NaNO_3$ + 15 ml water (*p*H = 4.15)	+0.5 to +1.6	−0.6 to −1.9	Cationic	Cationic
(5) 25 ml 2*M* HCOONa + 15 ml 2*M* HCOOH + 50 ml 1*M* $NaNO_3$ + 10 ml water (*p*H = 3.97)	+0.2 to +1.1	−0.9 to −2.6	Cationic	Cationic
(6) 25 ml 2*M* HCOONa + 20 ml 2*M* HCOOH + 50 ml 1*M* $NaNO_3$ + 5 ml water (*p*H = 3.85)	+0.1 to +1.1 and −0.8 to −1.6	−1.1 to −2.6	Cationic	Cationic
(7) 25 ml 2*M* HCOONa + 25 ml 2*M* HCOOH + 50 ml 1*M* $NaNO_3$ + (*p*H = 3.75)	+0.1 to 1 and −1.9 to −2.7	−1 to −3.1	Cationic	Cationic

(Formate concentration and ionic strength constant, *p*H is variable)

All electrolytes in Table 2 have the same *p*H and it will be equal to the pK_a of formic acid because of the same concentration of salt and acid. Hence, *p*H is 3.75 in all the cases and

$$[H^+_a] = 18\times10^{-5} \text{ g-ion/litre}$$

Concentration of H^+ is essential to calculate the ionic strength of the electrolyte because formic acid is a weak acid as it does not undergo complete dissociation.

Table 2 shows that Fe(III) ion behaves as an anionic complex throughout the concentration range (1*M* to 0.2*M*) of sodium formate when the *p*H and the ionic strength of the carrier electrolyte are constant. But at low concentration (0.1*M*) of Na-formate, Fe(III) moves towards the cathode. Cu(II) forms anionic complex when concentration of sodium formate is high (1*M* to 0.5*M*) but below this concentration Cu(II) forms cationic species with carrier electrolyte under the same condition. In the case of Ni(II) and Co(II), both the ions move as cationic species throughout the experiment. Hence it can be concluded that the relative stability of Fe(III)-formato complex is more than that of Cu(II)-formato complex.

Table 3 indicates that Fe(III) forms anionic complex with the carrier electrolyte throughout the experiment (*p*H 5.15-3.75) but at *p*H 3.85 and 3.75, Fe(III) forms both anionic and cationic species when ionic strength of the electrolyte and Na-formate concentration are constant. Cu(II) forms anionic formato complex at *p*H 5.15-4.45 and forms cationic species at *p*H 4.15-3.75. In the case of Ni(II) and Co(II) both the ions move towards the cathode throughout the experiment.

From the experimental data it can be said that the Fe(III)-formato complex is very stable but Cu(II) formato complex is not so stable. So the relative stability of Fe(III)-formato complex is higher than that of Cu(II)-formato complex.

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Solvent Extraction of Thorium with Liquid Cation Exchanger (Versatic 10)**

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THE synthetic carboxylic acids, Versatic 911 and Versatic 10, have been shown to be a promising extractant for large scale processing of transition metals[1]. A number of papers have appeared on the extraction of metals with versatic acids[2-8] and the composition of the extracted species has also been investigated[4-6]. Flett[7] reported its use for the extraction of metal in commercial plant. This communication reports the extraction of thorium(IV) and determination of probable composition of the extracted species using Versatic 10 in benzene as extractant. Quantitative extraction from 0.1 M acetate solution was achieved in the pH range 4.0-5 2. Thorium was separated from most of the rare earth elements, having separation factor, D_{Th}/D_M, in the order of 10^4. The probable composition of the extracted species $ThR_4.2RH$ (RH = Versatic 10) was deduced from the extraction data.

Experimental

Apparatus and reagents : Elico pH meter (Elico, Model LI-10, Hyderabad, India) was used for measurement of pH.

Versatic 10 (Shell Chemical Co., London), a mixture of branched C_{10} isomeric tertiary monocarboxylic acids[9], was used in conjunction with benzene, without further purification. The purity and concentration of Versatic 10 was 99% and 5.28 M, respectively.

Thorium acetate solution (1 04 mg/ml) was prepared by dissolving 3.8 g $Th(NO_3)_4.6H_2O$ (E. Merck) in deionized water followed by precipitation of the metal hydroxide and subsequent dissolution in 0.2 M acetic acid. The solution was standardised by complexometric titration with EDTA (disodium salt) using xylenol orange indicator. All other chemicals and solvents were of analytical grade.

Extraction procedure : The aqueous phase (20 ml) containing 2.2×10^{-3} M thorium was equilibrated with 10 ml of 0.88 M Versatic 10 in benzene for 5 min. Distribution ratio reached a constant value within 2 min of shaking, so contact time of 5 min was used in all the experiments. NaOH solution was used for adjustment of pH. All the extraction experiments were carried out at 30±1° and the ionic strength was maintained at 0.1 M with acetic acid. The two layers were allowed to settle for 5 min. The aqueous phase separated and the equilibrium pH measured. The aqueous phase was washed with 5 ml benzene to remove entrained solvent and the benzene extract was mixed with the separated organic phase. The amount of thorium present in the aqueous phase was estimated by titration with EDTA. The metal ion from the organic phase was stripped with 2N HNO_3 (20 ml) and the acid extract was washed with 5 ml benzene to remove the entrained solvent present. The amount of thorium extracted was estimated by titrating the acid extract with EDTA.

Results and Discussion

The extraction of thorium(IV) from 0.1 M acetate solution with Versatic 10 was performed at various pH. With constant extractant concentration (0.88M) and constant metal concentration ($2.2\times10^{-3}M$) extraction of thorium increased with increased pH and became quantitative at pH 4-5.2. The optimum pH range for quantitative extraction is 4-5.2. The equilibration time was determined by varying the contact time from 0 5 min to 10 min. The distribution ratio, D, reached a constant value within 2 min and back extraction was completed within 5 min. However, contact time and stripping time was kept at 5 min in all the experiments. Various diluents, viz., benzene, toluene, xylene, carbon tetrachloride, diisopropyl ether, chloroform and butanol were tried on the extraction of thorium under the optimum conditions. Quantitative extraction of thorium was achieved in all the cases except diisopropyl ether. In case of diisopropyl ether emulsion formation took place. Some saturation experiments were undertaken at pH 4.9 to examine the practical applicability of the proposed method for large scale extraction of thorium. 25 5 g/l of thorium could be extracted (94.5%) in a single step at pH 4.9. Further increase of thorium in the aqueous phase leads to difficulty in phase separation.

Probable extraction mechanism : The acetate ion dependency on extraction was investigated by performing the extraction at constant pH, constant metal ion concentration ($2 2\times10^{-3}M$) and constant Versatic 10 concentration (0.88M). Results show that increase of acetate ion in the aqueous phase leads to reduced extraction. This was probably due to formation of less extractable thorium acetate complexes in the aqueous phase. The plot of log D against log [acetate] was linear with a slope of −4 1, indicating the release of four acetate ions in the extraction process. The plot of log D against log [Versatic 10] was linear with a slope of 2.9. Versatic acids are known to exist as dimer in nonpolar solvent such as benzene[8]. The probable extraction mechanism, can therefore be expressed as :

$$Th^{4+} + \overline{3R_2H_2} \rightleftharpoons \overline{ThR_4.2RH} + 4H^+$$

where R_2H_2 represents the dimeric form of Versatic 10 in benzene and the barred species are in the organic phase.

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Extractive separations: Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+} and Hg^{2+} did not interfere in the extraction of thorium(IV). In all these cases, separations were achieved simply by controlling the *p*H (*p*H=4.6) of the aqueous phase during extraction. Separation factor, D_{Th}/D_{M}, in the order of 10^4 was achieved in all these cases. Only in the case of mercury, two consecutive equilibrations were required at *p*H 4.3. The interfering ions were Ce^{4+}, Pb^{2+} and U^{6+}. In order to assess the possible analytical applications, the proposed method was applied for the extraction of thorium(IV) from several synthetic mixtures prepared by mixing 5 mg of each metal [Th(IV) + Ca(II)+Ba(II); Th(IV)+ La(III) + Pr(III) + Nd(III); Th(IV) + Sm(III) + Gd(III) + Tb(III); Th(IV) + Zn (II) + Cd (II) + Hg(II)]. In most of the cases quantitative recovery of thorium was achieved. Extraction experiments were carried out at *p*H 4.6 using 0.88 *M* Versatic 10 (10 ml) in benzene.

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Effect of Different Groups on Cyclopentadienyl Ring on the Stability of Titanium-Cyclopentadienyl Bond

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Reactions of $ABTiCl_2$ (A = cyclopentadienyl and B = methylcyclopentadienyl or indenyl) with sodium salts of dithiocarbamic acids, $Na(S_2CNRR')$ (R = R' = CH_3, C_2H_5, i-C_3H_7; or R = CH_3 and R' = C_6H_5) have been carried out in the molar ratio of 1 : 3. It was found that in case of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2$ the cyclopentadienyl ring was knocked off resulting in the formation of $(\eta^5\text{-}CH_3C_5H_4)Ti(S_2CNRR')_3$, whereas, in case of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2$ the indenyl ring was knocked off resulting in the formation of $(\eta^5\text{-}C_5H_5)Ti(S_2CNRR')_3$. A suitable explanation for this observation has been proposed.

SUBSTITUTION on Cp ring affects the stability of titanium-cyclopentadienyl bond i.e., in case of $(\eta^5\text{-}C_5H_5)TiCl_3$, cyclopentadienyl ring is lost by alkaline hydrolysis, whereas $[(\eta^5\text{-}CH_3)_5C_5]TiCl_3$ is converted only to $[\{\eta^5\text{-}(CH_3)_5C_5\}Ti(OH)]_n$[1]. In the other case, unlike $(\eta^5\text{-}Cp)_2Ti(CH_3)_2$, the yellow pentane solutions of $[(\eta^5\text{-}(CH_3)_5C_5]_2Ti(CH_3)_2$ were found to show no reactivity towards H_2 even at 100 atm pressure[2]. Recently, it has been established that in the reaction of $(\eta^5\text{-}C_5H_5)_2MCl_2$ or $(\eta^5\text{-}CH_3C_5H_4)_2MCl_2$, (M = Ti, Zr or Hf), with sodium dithiocarbamates in the ratio of 1 : 3, one cyclopentadienyl or methylcyclopentadienyl ring is knocked off resulting in the formation of $(\eta^5\text{-}C_5H_5)M(DTC)_3$ or $(\eta^5\text{-}CH_3C_5H_4)M(DTC)_3$[3-13].

In the present communication reactions of $ABTiCl_2$, [A = $\eta^5\text{-}C_5H_5$, B = $\eta^5\text{-}CH_3C_5H_4$ or $\eta^5\text{-}C_9H_7$(indenyl)], with $Na(S_2CNRR')$, (R = R' = CH_3, C_2H_5, i-C_3H_7; or R = CH_3, R' = C_6H_5), have been studied with a view to ascertain the effect of the different groups present on cyclopentadienyl ring on the stability of titanium-cyclopentadienyl bond. In the case of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2$, cyclopentadienyl ring is knocked off indicating that the $-CH_3$ group present on the cyclopentadienyl ring imparts stability to titanium-cyclopentadienyl bond, whereas in the case of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2$, indenyl ring is knocked off thereby indicating that the presence of phenyl ring fused to cyclopentadienyl ring (in indenyl) makes the titanium-cyclopentadienyl bond fragile.

Experimental

Reagents and general techniques : $[\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2$ was prepared by the reaction of $\eta^5\text{-}CpTiCl_3$ and $(\eta^5\text{-}CH_3C_5H_4)Tl$ (I) in 1 : 1 molar ratio in THF. $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2$ was prepared by the reaction of $\eta^5\text{-}CpTiCl_3$ and sodium indenide in 1 : 1 molar ratio in THF[13]. Sodium salts of dithiocarbamic acids were prepared as described by Klopping and Kerk[14] and dried before use. All the organic solvents used were predried and well purified.

Preparation of the complexes :

[A] *Reaction of sodium salt of N,N-dimethyldithiocarbamic acid on $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2$:* $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2$ (0.2630 g; 0.001 mole) was refluxed with $Na[S_2CN(CH_3)_2]$ (0.4290 g; 0.003 mole) in CH_2Cl_2 (50 ml) for 10 hr. The reaction mixture was cooled and filtered. The volume of the filtrate was reduced to ~10 ml *in vacuo* and petroleum ether (60-80°) was added dropwise to precipitate the complex. The precipitate was filtered, dried and recrystallized from 1 : 1 mixture of dichloromethane and petroleum ether to isolate the yellow orange product, $(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(CH_3)_2]_3$ in > 90% yield. Reactions of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2$ with other dithiocarbamates, i.e., $Na(S_2CNRR')$, (R = R' = C_2H_5, i-C_3H_7; or R = CH_3, R' = C_6H_5), in 1 : 3 molar ratio were carried out in similar manner and yielded corresponding mono(methylcyclopentadienyl) *tris*dithiocarbamatotitanium (IV) complexes in > 90% yield.

[B] *Reaction of sodium salt of N,N-disubstituted dithiocarbamic acid on $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2$:* Reactions of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2$ with $Na(S_2CNRR')$, (R = R' = CH_3, C_2H_5, i-C_3H_7; or R = CH_3, R' = C_6H_5), in 1 : 3 molar ratio were also carried out in the manner as described in [A] to yield the respective mono(cyclopentadienyl) *tris*dithiocarbamatotitanium(IV) complexes in > 90% yield.

Physico-chemical measurements : The ir spectra in the region 4000-250 cm^{-1} were recorded on Perkin-Elmer 621 grating spectrophotometer. The ^1H nmr spectra were recorded at ambient temperature ~30° in $CDCl_3$ on a Varian A-60 NMR spectrometer at a sweep width of 500 Hz using TMS as an internal standard. Molecular weight of

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TABLE 1—PHYSICAL DATA FOR $(\eta^5\text{-}CH_3C_5H_4)Ti(S_2CNRR')_3$ AND $(\eta^5\text{-}C_5H_5)Ti(S_2CNRR')_3$

Complex	Molar conductivity $ohm^{-1}cm^2mole^{-1}$	Concentration mM	Molecular weight Found (Calcd.)	Analysis % Found (Calcd.) C	H	N	Ti	m.p. and colour
$(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(CH_3)_2]_3$	0.22	0.5	490 (487)	40.1 (37.0)	5.2 (5.1)	8.5 (8.6)	9.8 (9.9)	160° Yellow
$(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(C_2H_5)_2]_3$	0.20	0.5	565 (571)	43.8 (44.1)	6.4 (6.5)	7.2 (7.3)	8.1 (8.4)	158° Yellow
$(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(i\text{-}C_3H_7)_2]_3$	0.23	0.4	660 (655)	48.9 (49.5)	7.6 (7 5)	6.2 (6.4)	7.4 (7.3)	170° Yellow orange
$(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(CH_3)(C_6H_5)]_3$	0.25	0.5	690 (673)	54.2 (53.5)	4.5 (4.6)	6.5 (6.2)	7.3 (7.1)	90° Orange yellow
$(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$	0.22	0.5	431 (473)	35.2 (35.5)	4.7 (4.86)	8.7 (8.88)	10.3 (10.15)	240° Yellow orange
$(\eta^5\text{-}C_5H_5)Ti[S_2CN(C_2H_5)_2]_3$	0.21	0.5	512 (557)	43.2 (43 09)	6.1 (6.26)	7.2 (7.54)	8.8 (8.62)	250° Yellow orange
$(\eta^5\text{-}C_5H_5)Ti[S_2CN(i\text{-}C_3H_7)_2]_3$	0.21	0.5	655 (641)	49.1 (48.7)	7.4 (7.3)	6.7 (6.5)	7.3 (7.5)	149° Orange yellow
$(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)(C_6H_5)]_3$	0.20	0.5	668 (659)	53.5 (52.8)	4.3 (4.4)	6.5 (6.37)	7.4 (7.28)	101° Orange

TABLE 2—PROTON CHEMICAL SHIFT (τ VALUES IN ppm) AT ~30° IN $CDCl_3$

Complex	$CH_3C_5H_4$ or C_5H_5 ring protons	CH_3 protons of $CH_3C_5H_4$	(S_2CNRR') protons $-C_6H_5$ protons	→CH protons	$-CH_2$ protons	$-CH_3$ protons
$(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(CH_3)_2]_3$	4.43(t), 4.00(t)	7.75	—	—	—	6.76(d) (5 . 1)
$(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(C_2H_5)_2]_3$	4.58(t), 4.1(t)	7.80	—	—	6.325(q)	8.83(t)
$(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(i\text{-}C_3H_7)_2]_3$	4.48(t), 4.05(t)	7.77	—	5.28(m)	—	A 8.66(d) (2 : 1); B 8.61(d) (2 . 1)
$(\eta^5\text{-}CH_3C_5H_4)Ti[S_2CN(CH_3)(C_6H_5)]_3$	4.55(t), 4.17(t)	7.85	2 89(d) (2 . 1)	—	—	6.51(d) (2 . 1)
$(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)_2]_3$	4 1	—	—	—	—	6.76(d) (5 ; 1)
$(\eta^5\text{-}C_5H_5)Ti[S_2CN(C_2H_5)_2]_3$	3.78	—	—	—	6.975(q)	8.53(t)
$(\eta^5\text{-}C_5H_5)Ti[S_2CN(i\text{-}C_3H_7)_2]_3$	4.05	—	—	5.52(m)	—	A 8.64(d) (2 : 1); B 8.57(d) (2 : 1)
$(\eta^5\text{-}C_5H_5)Ti[S_2CN(CH_3)(C_6H_5)]_3$	3.73	—	2.59(d) (2 : 1)	—	—	7.975(d) (2 . 1)

m = multiplet, q = quartet, t = triplet, d = doublet, A and B are the two doublets of equal intensity.

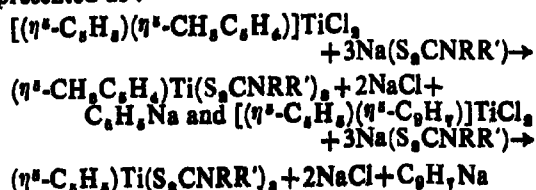
the complexes were determined on Gallenkamp ebullioscope in benzene and conductivity measurements were carried out in nitrobenzene using Elico CM82T conductivity bridge.

Results and Discussion

The reactions of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2$ or $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2$ with $Na(S_2CNRR')$ ($R=R'=CH_3$, C_2H_5, $i\text{-}C_3H_7$; or $R=CH_3$ and $R'=C_6H_5$) in 1 : 3 molar ratio have been studied in nonaqueous medium. These reactions may be represented as :

$$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2 + 3Na(S_2CNRR') \rightarrow (\eta^5\text{-}CH_3C_5H_4)Ti(S_2CNRR')_3 + 2NaCl + C_5H_5Na$$

and

$$[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2 + 3Na(S_2CNRR') \rightarrow (\eta^5\text{-}C_5H_5)Ti(S_2CNRR')_3 + 2NaCl + C_9H_7Na$$

These complexes are yellow orange to orange in colour and are insoluble in H_2O and petroleum ether but are highly soluble in $CHCl_3$, CH_2Cl_2, C_6H_6, CS_2, CH_3COCH_3 and THF. They are thermally stable but slowly hydrolyse on exposure to moist air. The conductivity measurements in nitrobenzene and molecular weight determinations in benzene indicate that the complexes are non-electrolytic monomers. Physical data for these complexes are given in Table 1. These complexes have also been prepared previously by the reaction of $(\eta^5\text{-}CH_3C_5H_4)_2TiCl_2$ or $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $Na(S_2CNRR')$[8-10].

Infrared spectra : The ir spectrum of each of these complexes shows only one $\nu C{=}N$ at ~1505 cm^{-1} and only one $\nu C{=}S$ at ~1000 cm^{-1}. The pentahapto cyclopentadienyl ring in the complexes $(\eta^5\text{-}C_5H_5)Ti(S_2CNRR')_3$ is identified by the characteristic ir bands viz., C-H stretching at ~2925 cm^{-1},

C–C stretching at ~1430 cm^{-1}, symmetric ring breathing at ~1120 cm^{-1}, C–H asymmetric in plane deformation at ~1010 cm^{-1} and C–H out of plane deformation at ~845, ~800 cm^{-1}. The presence of pentahapto methylcyclopentadienyl ring in the complexes $(\eta^5\text{-}CH_3C_5H_4)Ti(S_2CNRR')_3$ is identified by the characteristic ir bands viz., C–H stretching (ring) at ~3100 cm^{-1}, C–C stretching at ~1435 cm^{-1}, symmetrical ring breathing ~1125 cm^{-1}, C–H asymmetric in plane deformation at ~1035 cm^{-1} and C–H out of plane deformation at ~865, ~825 cm^{-1}.

The ir data for these complexes are similar to those already prepared[6-10]. Therefore, the dithiocarbamato ligands in these complexes are bidentate and a coordination number of 'seven' may be assigned to titanium as already discussed[6-10].

^{1}H nmr spectra : The ^{1}H nmr data for these complexes are given in Table 2 and are similar to those already reported[6-10]. Therefore, these complexes are stereochemically rigid heptacoordinate chelates which assume different geometries[6-10].

Effect of the different groups present on the cyclopentadienyl ring on the stability of titanium-cyclopentadienyl ring : The reactions of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)]TiCl_2$ or $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2$ with sodium salts of N,N-disubstituted dithiocarbamic acids in 1 : 3 molar ratio yield *tris*dithiocarbamato complexes and one ring out of the two attached to titanium is knocked off. Naturally, the one having weaker titanium ring bond will be knocked off leaving the other ring having comparatively stronger bond with titanium.

In the case of the reaction of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3\text{-}C_5H_4)]TiCl_2$ with sodium dithiocarbamate, the cyclopentadienyl ring is knocked off. It clearly indicates that $(\eta^5\text{-}CH_3C_5H_4)$-Ti bond is stronger than $(\eta^5\text{-}C_5H_5)$-Ti bond. In fact, the electron releasing property of the methyl group present on the cyclopentadienyl ring in methylcyclopentadienyl group increases the electron density in the ring, imparting thereby additional stability to the titanium-methylcyclopentadienyl bond. Thus, as compared to titanium-methylcyclopentadienyl bond, titanium-cyclopentadienyl bond becomes relatively fragile and can be knocked off by dithiocarbamate ligand.

On the other hand in the case of the reaction of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]TiCl_2$ with sodium dithiocarbamates, the indenyl ring is knocked off. It indicates that $(\eta^5\text{-}C_9H_7)$-Ti bond is weaker than $(\eta^5\text{-}C_5H_5)$-Ti bond. In fact the electron withdrawing property of C_6H_5 ring fused to cyclopentadienyl ring (in indenyl ring) decreases the electron density of the cyclopentadienyl ring of the indenyl group. Thus, $(\eta^5\text{-}C_9H_7)$-Ti bond becomes weaker as compared to $(\eta^5\text{-}C_5H_5)$-Ti bond. Therefore, preferential removal of indenyl ring by dithiocarbamate ligand takes place during the formation of *tris*dithiocarbamato complexes.

It is, therefore, concluded that the electron releasing groups present on cyclopentadienyl ring increases the stability of titanium-cyclopentadienyl bond whereas the presence of electron withdrawing groups on cyclopentadienyl ring makes the titanium-cyclopentadienyl bond fragile and exchangeable. The order of stability is $\eta^5\text{-}CH_3C_5H_4\text{-}Ti > \eta^5\text{-}C_5H_5\text{-}Ti > \eta^5\text{-}C_9H_7\text{-}Ti$. During the reaction with DTC, one ring always remains attached with titanium. The fact has been ascertained through ^{1}H nmr spectra of the resultant products.

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Some Lanthanide-EDTA Ternary Complexes with Catechol, Resorcinol and Phloroglucinol

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The proton-ligand stability constants of catechol, resorcinol and phloroglucinol and the metal-ligand stability constants of the 1 : 1 binary complexes, ML ($M=La^{3+}$, Ce^{3+}, Pr^{3+}, Nd^{3+} or Sm^{3+} and L=cat, res or phl) and 1 : 1 : 1 ternary complexes, MAL ($M=La^{3+}$, Ce^{3+}, Pr^{3+}, Nd^{3+} or Sm^{3+}; A=edta; L=cat, res or phl) have been determined at 28° and $\mu=0.2M$ ($NaClO_4$) using Irving-Rossotti *p*H-titration technique. The stability constant values have been found to lie in the order $\log K^M_{MA} \gg \log K^M_{ML} > \log K^{MA}_{MAL}$. The ΔF and $\Delta \log K$ values have been calculated. The stability of the complexes ML as well as MAL is found to be in the sequence cat > res > phl with respect to the secondary ligands, and $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+}$ with respect to the metal ions.

Validity of Born's relation has been tested for the ternary complexes MAL. The $\log K^{MA}_{MAL}$ values have been correlated with the standard entropies, standard electrode-potentials and ionic potentials of the lanthanides.

The $\log K^{MA}_{MAL}$ vs $\log K^M_{ML}$ or $\log K^M_{MA}$ plots are found to be linear. Comparison of the experimental values of $\log K^{MA}_{MAL}$ for catechol with the literature values for some corresponding cdta and nta ternary lanthanide complexes reveals the stability sequence nta > edta > cdta.

STABILITY constants of 1 : 1 : 1 ternary complexes of the type [M(II)-edta-cat][1], where $M(II)=Ni^{2+}$, Cu^{2+}, Zn^{2+} or Cd^{2+}, [Ni(II)-*o*-phen-cat][2], [Ni(II)-dipy-cat][3] and [M(III)-A-cat][4], where $M(III)=La^{3+}$, Pr^{3+} or Nd^{3+} and A=cdta or nta, have been determined by earlier workers. Stability constants of binary lanthanide-catechol chelates have also been reported recently[5].

The present work deals with the determination of the stability constants of 1 : 1 binary and 1 : 1 : 1 ternary lanthanide complexes using edta as a primary ligand and catechol (cat), resorcinol (res) or phloroglucinol (phl) as a secondary ligand. Some stability correlations have also been attempted.

Experimental

Standard solutions of catechol, resorcinol and phloroglucinol were prepared in double distilled water by direct weighing. The lanthanide solutions were prepared by dissolving the nitrates of La(III), Ce(III) and Sm(III) in water. Pr(III) and Nd(III) oxides were dissolved in minimum quantity of perchloric acid, excess of which was carefully evaporated and checked before-hand so as to eliminate the possibility of any extra acid in the metal ion solution. EDTA was used as its disodium salt, the two remaining protons were also taken care of.

The usual titration sets i.e. (i) acid, (ii) acid+secondary ligand (L), (iii) acid+L+metal ion (M) for the binary complexes; and (i) acid+primary ligand (A)+M, (ii) acid+L, (iii) acid+M+A+L for the ternary complexes were prepared. The ionic strength was maintained at $\mu=0.2M$ ($NaClO_4$) Dilute solutions ($10^{-3}M$) were used to avoid the possibility of formation of polynuclear species. The sets were titrated *p*H metrically against 0.2*M* carbonate free NaOH, at 28° using Irving-Rossotti titration technique[6].

A digital *p*H-meter (model Elico-LI-120) was used. Reproducible *p*H readings were used for calculations. Plots of *p*H vs alkali added for 1 : 1 binary complexes of La(III) with cat, res and phl and those for the corresponding 1 : 1 : 1 ternary complexes were worked out.

Results and Discussion

The calculated values of proton-ligand stability constants $\log K^H_1$ and $\log K^H_2$ of the secondary ligands are recorded in Table 1. The metal-ligand stability constants of 1 : 1 binary complexes with

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS OF THE SECONDARY LIGANDS

Ionic strength $\mu=0.2M(NaClO_4)$, Temp.=28°

Ligand	$\log K^H_1$	$\log K^H_2$	$\log \beta$
Catechol	9 20	11.70	20.90
Resorcinol	9.07	11.07	20.14
Phloroglucinol	8.30	9.76	18.06

TABLE 2—METAL-LIGAND STABILITY CONSTANTS OF 1 : 1 BINARY AND 1 : 1 : 1 TERNARY LANTHANIDE COMPLEXES

Ionic strength $\mu = 0\ 2M(NaClO_4)$. Temp. = 28°

Metal ion	$\log K^{M}_{MA}$	Catechol				Resorcinol				Phloroglucinol			
		$\log K^{M}_{ML}$	$\log K^{MA}_{MAL}$	$-\Delta \log K$	$-\Delta F^{*}$	$\log K^{M}_{ML}$	$\log K^{MA}_{MAL}$	$-\Delta \log K$	$-\Delta F^{*}$	$\log K^{M}_{ML}$	$\log K^{MA}_{MAL}$	$-\Delta \log K$	$-\Delta F^{*}$
La^{3+}	9.31	8 55 (±0.03)	6.20 (±0.03)	2 35	8 59	4.45 (±0.03)	2 10 (±0.04)	2.35	2 91	3 50 (±0.02)	2 20 (±0 03)	1.30	3 05
Ce^{3+}	9.02	8.65 (±0 04)	6.50 (±0.02)	2.15	9 01	4 55 (±0.02)	2.20 (±0.04)	2 35	3 05	3 75 (±0.04)	2.40 (±0 03)	1.35	3.33
Pr^{3+}	9.96	8.90 (±0.04)	6.70 (±0.03)	2.20	9.29	5.05 (±0.04)	2.35 (±0 03)	2.70	3.26	3.90 (±0 03)	2.50 (±0.05)	1.40	3.47
Nd^{3+}	10.56	9.10 (±0.07)	7 00 (±0.05)	2.10	9 70	5 35 (±0.07)	2.50 (±0 05)	2.85	3.47	4.00 (±0.07)	2.60 (±0.02)	1.40	3.60
Sm^{3+}	11.02	9.20 (±0.03)	7.45 (±0.05)	1.75	10.32	5.95 (±0.03)	3.05 (±0.03)	2.90	4.23	4.20 (±0.02)	2.70 (±0.02)	1.50	3.74

* $-\Delta F$ = K cal mole^{-1}.

A ($\log K^{M}_{MA}$) and L ($\log K^{M}_{ML}$) and of 1 : 1 : 1 ternary complexes ($\log K^{MA}_{MAL}$) along with their standard deviations (in parentheses) are shown in Table 2. The $\Delta \log K$ values i.e. $\log K^{MA}_{MAL} - \log K^{M}_{ML}$ and the ΔF values for the ternary complexes ($\Delta F = -RT \log K^{MA}_{MAL}$) are also included in this table.

It was observed from the *p*H plots that the separation of secondary ligand curve from the acid curve took place at *p*H≈7 due to ionisation of the phenolic group in the relatively higher *p*H range. The values of $\bar{n}_H$ obtained in the range $0 < \bar{n}_H < 2$ have been used to calculate $\log K^{H}_{1}$ and $\log K^{H}_{2}$ for cat, res and phl. The values are in good agreement with those reported in literature[7,8]. The higher value of $\log K^{H}_{2}$ over that of $\log K^{H}_{1}$ may be due to lowering of the inductive effect in the second step of ionisation[9] and also hydrogen bonding[10]. The observed sequence of ligand basicity, cat > res > phl, is expected due to a greater proximity of the phenolic groups in catechol.

It was found that the binary complex curve practically overlapped the ligand curve in the lower buffer region, which minimised he possibility of formation of any protonated species[11]. The separation of the two curves occurred at *p*H≈5.5 to 6.0 indicating complexation. The $\bar{n}$ values have been calculated in the *p*H range where no precipitation was observed. The ternary complex curve separated at lower *p*H region from the curves of the primary complex and the secondary ligand indicating the formation of the ternary complex. This has been further confirmed by the non-superimposable[12] nature of the theoretical composite curve on the experimental curve of ternary complex. The ternary complex is obviously formed according to the scheme : M+A ⇌ MA ; MA+L ⇌ MAL.

A perusal of the values of stability constants (Table 2) shows that the general order is $\log K^{M}_{MA} \gg \log K^{M}_{ML} > \log K^{MA}_{MAL}$. The much higher value of $\log K^{M}_{MA}$ over that of $\log K^{M}_{ML}$ eliminates the possibility of ligand displacement, MA+L ⇌ ML+A, in the ternary systems. Any disproportionation of the ternary complex MAL is also discounted as the hexadentate nature of edta will not favour the formation of the species MA_2[13]. The lower values of $\log K^{MA}_{MAL}$ may be due to coulombic repulsion between the negatively charged primary complex MA, [Ln-edta]$^-$, and the incoming secondary ligand (L^- or L^{2-}). Steric repulsions and statistical considerations are also expected to contribute towards the lowering of $\log K^{MA}_{MAL}$ value as compared to $\log K^{M}_{ML}$. The $\Delta \log K$ values are consequently negative.

Calculation of % ionisation[14] reveals that the second phenolic-OH in res and phl is very little ionised (res ; 0.09-2.4% ; phl ; 0.2-24%) in the *p*H range used for calculations. It, therefore, appears reasonable to use only the $\log K^{H}_{1}$ value in these two cases for calculating the stability constants. The sequence of stability with respect to the secondary ligands for binary as well as ternary complexes has been found to be cat > res > phl, which is the order of ligand basicities. The variation of $\log K^{MA}_{MAL}$ for the lanthanides shows the expected trend $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+}$, which is the order of decreasing ionic radii of the metal ions. The relative complexing tendencies as measured by K^{M}_{MA}/K^{M}_{ML} are found to lie in the sequence phl > res > cat ; the variations in numerical values being large e.g., 10^6 to 10^1 for the La^{3+} complexes.

Unlike the '3d'-elements, the lanthanides are highly electropositive with large ionic radii and their $4f^n$ electrons are well shielded by the outer lying 5S and 5p orbitals from ligand perturbations. The metal-ligand bond should, therefore, be ionic with a minimal covalent contribution, if at all. Born relation[15] $E = z^2/2r\ (1-1/D)$ (where E = energy of complexation, z = charge and r = ionic radius of the metal ion) has been tested for the present series of ternary complexes. Plots of $\log K^{MA}_{MAL}$ vs z^2/r were found to be curved, which may be due to partial covalent nature[16] of the bond and varying degrees of stabilisation caused by the ligand field. Similar

observations[17-19] have been noted for some other lanthanide complexes.

The log K^{MA}_{MAL} values were plotted against log K^{M}_{MA} and log K^{M}_{ML} and produced almost linear plots indicating similarity in bonding in the binary and ternary complexes. Slight deviations from linearity may be due to additional steric effects involved in the formation of the ternary complexes.

The variation of log K^{MA}_{MAL} with the standard entropies, S°, of the lanthanides[20] showed a linear increase in the stability constant with S° indicating that the changes in free energy during complexation are essentially changes in entropy. A similar trend has been observed for the 1:1 Ln-edta complexes by Foreman and Smith[21]. The stability constants of the ternary complexes increased regularly with increase in the ionic potentials of the lanthanides. This trend is expected in view of the decreasing ionic radii of tervalent lanthanide cations. Standard electrode potentials, E°, of the lanthanides plotted against the stability constants yielded a linear plot. The free energy corresponding to the standard electrode potential comprises mainly the heat of formation of the bare Ln^{3+} ion and its heat of hydration. The latter being the heat of ligation of water molecules, one may expect a gradual increase in log K^{MA}_{MAL} value with decrease in the numerical value of E° (with increasing value of $4f^n$) for the lanthanides.

It is interesting to note an expected trend between our values of log K^{MA}_{MAL} and the reported values for similar ternary systems as shown below :

System	log K^{MA}_{MAL}			Reference
	La^{3+}	Pr^{3+}	Nd^{3+}	
Ln-cdta-cat	4.83	5 69	6 10	4
Ln-edta-cat	6.20	6 70	7 00	Present work
Ln-nta-cat	6.30	6.98	7 36	4

The increase in log K^{MA}_{MAL} values in the order cdta < edta < nta may be due to (i) greater coulombic repulsion in the case of cdta and edta between the primary and secondary ligands than in the case of nta, (ii) availability of more coordination sites for the secondary ligand in the case of nta than for cdta and edta and (iii) between edta and cdta, greater loss of conformational freedom in the case of cdta.

The only comparable values of log K^{MA}_{MAL} for the '3d'-elements as reported by Bhattacharya *et al*[1] are [Ni(II)-edta-cat], 4.44 ; [Cu(II)-edta-cat], 7.01 and [Zn(II)-edta-cat], 3.73. The higher value for the Cu(II) complex may be attributed chiefly to Jahn Teller distortion resulting in increased binding energy.

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Metal Ion Interactions with the Constituents of Nucleic Acid. Part-I : Metal-Adenine Complexes

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Metal-adenine complexes of the type $[Cd(AdH)_2Cl_2]$, $[Hg_2Cl_2Ad_2(AdH)]$, $[Pd_2Cl_2Ad_2(AdH)]2H_2O$ and $[UO_2(Ad)_2(H_2O)_2]H_2O$ have been isolated and characterised by analytical, infrared and TGA data. The AdH (neutral adenine) is probably unidentate in the Cd complex whereas in the Hg and Pd complexes, it functions probably as a bidentate bridging ligand, linking two metal ions. In the case of the Pd complex, Ad coordinates through C(6) NH_2 and N(7) but in all other cases possibly through N(3) and N(9) atoms.

THE biologically important intermolecular transfer of a phosphoryl group of adenosine triphosphate is an enzymic process with an absolute metal ion requirement. The non-enzymic transphosphorylation occurring between ATP and orthophosphate ion is also catalysed by bivalent metal ions, notably Mn^{2+}, Ca^{2+} and Cd^{2+} [1]. In a recent publication[2] we described the synthesis and characterisation of some metal-ATP complexes with particular emphasis on the binding sites. Adenine, one of the constituent bases of nucleic acids and the constituent base of ATP, is known[3] to enter into metal coordination either as a neutral molecule, AdH, or as a monoanion, Ad [by the deprotonation of N(9) i.e. the imino nitrogen]. In acid medium the base also coordinates as adeninium cation, AdH_2^+, where apart from N(9) [where one proton normally resides in free neutral adenine but if this nitrogen is linked with metal on coordination, the proton shifts to N(7)[4]], N(1) is also protonated[4,5].

The earlier work[6,7] regarding the preparation of the Au(III) adenine complex in dil HCl medium probably involves adenine in the form of the cation AdH_2^+. Only comparatively recently the Cu(II), Zn(II) and Pt(II) complexes with adenine have been isolated and their structures studied[8-10]. In this paper, we report the complexes of adenine with Cd(II), Hg(II), Pd(II) and UO_2(II).

Experimental

Preparation of the complexes : The Cd(II), Hg(II) and Pd(II) complexes are prepared by adding an aqueous solution of adenine in twice molar proportion to the respective metal chloride solution in water (aqueous NaCl in the case of $PdCl_2$). The precipitated solids (the pH of the medium after the precipitation of the complexes remains at 5) were washed with hot water, ethanol and ether and dried in vacuum.

In the case of dioxouranium(VI) complex, the aqueous solution of $UO_2(NO_3)_2.6H_2O$ and adenine were mixed in 1 : 2 molar ratio but the resultant solution was clear. The pH was raised to 5 by adding NaOH solution and the precipitated solid was washed and dried as in the other cases.

The compounds are insoluble in water as well as in all organic solvents.

Materials and methods : All chemicals used were of analytical grade. The infrared spectra (4000-200 cm^{-1}) as CsI pellets were recorded in a Perkin-Elmer Model 597 IR spectrophotometer. The water content and the decomposition temperatures were followed from the TGA curves[2].

Results and Discussion

The composition of the complexes and their analytical data are recorded in Table 1. The composition of the complexes, suggested on the basis of their analytical data is further corroborated by their infrared vibrational frequencies. In molecules like adenine, the intensity of the νNH_2 bands ($\sim$3300 cm^{-1}) is expected[11] to be not much greater than that of the νNH($\sim$3150 cm^{-1}). The position and relative intensities of the infrared bands may therefore be considered here as reasonable guide in deciding ligand type (neutral, anionic or cationic) and the probable binding sites. Making proper allowance for any intermolecular hydrogen bonding (specially in the free adenine molecule) and roughly analysing the overlapping NH_2 and NH bands as per Gausian method, it appears that in adenine (3250, 3050) the intensity of the said bands are in the ratio 1 : 1 and so also in the Cd compound (3300, 3135), but in the Hg compound (3325, 3050) the intensity of the former band is roughly double of that of the latter. These observations support the suggested compositions. Strong water absorption of the uranium compound as well as the medium intensity broad water band in the palladium complex frustrate such an attempt.

Comparing the positions of the four δNH_2 bands[12] in free adenine [1675 (s), symmetric in

TABLE 1—THE COMPOSITION, COLOUR, ANALYTICAL AND THE INFRARED DATA OF THE COMPLEXES

Compounds	Colour	Analysis%				(M – Cl)* cm^{-1}	(M – N)† cm^{-1}
		M Found (Calcd.)	N Found (Calcd.)	Cl Found (Calcd.)	H_2O Found (Calcd.)		
$CdCl_2(AdH)_2$	White	25 1 (24.8)	31.4 (30.9)	16.2 (15 7)	— —	340	542
$Hg_2Cl_2(AdH)(Ad)_2$	White	45.1 (45.8)	24 0 (24.0)	9 2 (8.1)	— —	338	545
$Pd_2Cl_2(AdH)(Ad)_2 2H_2O$	Yellow	29.4 (29.7)	28.3 (29.0)	10.4 (9.8)	4.7 (5 0)	325	445
$UO_2(Ad)_2 3H_2O$	Yellow	39.6 (40.1)	23 9 (23 6)	—	9.4 (9 1)	—	400

* Ref. 14c-16 , † Ref. 14a-18.

plane ; 1250 (m), asymmetric out of plane ; 910 (m), symmetric out of plane and 718 (m), asymmetric in plane deformation] and metal bound adenine (bands almost retain their positions), it is clear that
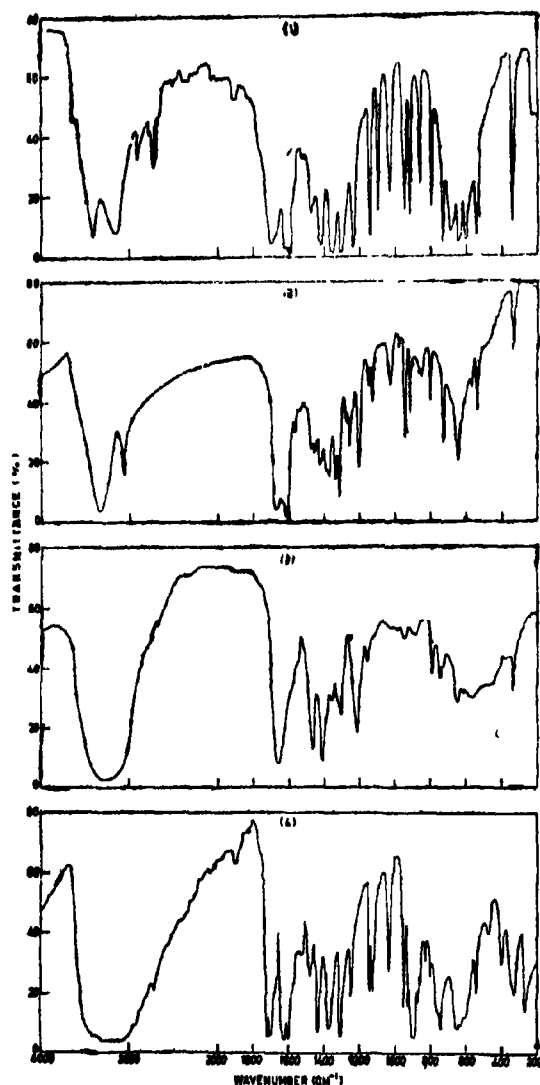
Fig. 1. The infrared spectra of (1) Cd complex, (2) Hg complex, (3) Pd complex and (4) UO_2 complex.

unlike the ATP complexes[8] [the bands described[8] as ν(CN) should be the symmetric in plane deformation of the NH_2 group in ATP and its complexes ; other δNH_2 bands are also there] the bands here do not undergo red shift (rather slightly blue shifted) on complexation, excepting in the case of Pd(II) complex, where it does [1645 (s), 1218 (m) ; 910 cm^{-1} band not observed]. This observation excludes the possibility of coordination through the C(6) NH_2 group in all the cases except that of the Pd(II), where the coordination definitely occurs through the said NH_2 group (see Fig. 1 for comparison). Modelling[18] indicates that involvement of the NH_2 group in coordination almost commits the participation of the N(7) of adenine. It may, therefore, be concluded that in the Pd(II) complex, Ad functions as a bidentate ligand linking through C(6) NH_2 and the N( ). Since in the said complex only a single type of NH_2 group is found from the ir data, the AdH probably functions as a bridging ligand between two Pd(II) groups—one linked to N(7) and the other to C(6) NH_2group (Fig. 2A). This contention is also supported by the ν(Pd – Cl) vibration (325 cm^{-1}) which indicates that chloride is present as a terminal ligand and not a bridging one[14c]. Similarly, in the Cd and Hg complexes the ν(M – Cl) band (Table 1) is indicative of terminal chloride ligands. No other band at still lower wave number regions is present in any of the cases (Fig. 1) thereby ruling out the possibility of a bridging M – Cl bond (see also refs. 15 and 16). It may also be quite partinent to mention here that $[Cu_2Ad_4]$ (prepared by the method of Weiss and Venner[8] and ir spectra recorded by us for comparison) complex is ir transparent in the region 400-200 cm^{-1}. However, in the Pd complex, as expected, the ring vibrations[11] of the purine ring is only very slightly modified after the involvement of the N(7) during metallation. In fact, the ring vibrations in the other cases (Cd^{2+}, Hg^{2+} and UO_2^{2+}) are a bit more modified. Based on these observations, and also the fact that in the latter two cases the NH_2 group remains free, it may be presumed that Ad^- in these cases functions as a bidentate ligand linking through N(3) and N(9) (Figs. 2B and 2C) as was confirmed in the case of Cu(II) by X-ray crystallography[8]. In the Hg(II)

complex, AdH probably acts as a bridging group linking through two Hg(II) ions, one with N(3) and the other with N(9), since here also only one type of NH_2 mode is present and the possibility of chlorine bridging is excluded from the far ir spectroscopy. Since the Cd(II) complex should be 4-coordinated, the AdH groups probably act here as a unidentate ligand linking through the N(9) (Fig. 2D), a site which might be preferred to N(3) (compare the nucleoside formation by linking through sugars at this point).

After a thorough comparison of the ir bands of adenine with those of the complexes, the ν(U – N) is assigned[17] at 400 while the ν(Pd – N) band at
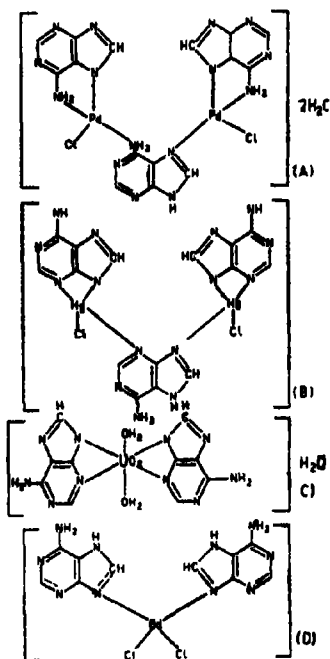
Fig. 2. The most probable structures of (A) Pd complex, (B) Hg complex, (C) UO_2 complex and (D) Cd complex.

445[14a] and the ν(Cd/Hg – N) bands in the vicinity of 540 cm^{-1} (Table 1). The Cd and Hg – N vibrations at higher wave numbers are also corroborated by earlier work on the N-chelates[14a]. The UO_2^{2+} complex contains two other bands, one at 320 and the other at 260 cm^{-1}. The latter band is assigned to the ν_2 (bending vibration)[19,20] of the UO_2^{2+} ion while the former is assignable to the ν(U – O) band arising out of the water ligands[14b,20-22].

TGA curves show that the water molecules in the Pd(II) complex and one of the water molecules in the UO_2^{2+} complex are lost well below 100° indicating that they are only weakly held in the lattice. Other water molecules present in the appropriate cases are lost just below 150° showing that they are coordinated. (However the δH_2O bands are entrapped within the strong δNH_2 absorption). All these confirm the suggested structures (Fig. 2).

The compounds are insoluble and the possibili of molecular polymerisation could not be ruled o Also, the insolubility of the complexes even DMSO did not permit any NMR work whi would have been more conclusive. They are pr pared under such a condition that isolation of goo crystals are impossible. So, presently, our kno ledge should remain limited to the formulation the most probable structures (Fig. 2A – 2D).

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Preparation and Characterization of Naphthoxides of Niobium(V) and Tantalum(V)

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Compounds of composition $MCl_n(ONp)_{5-n}$, where M=Nb or Ta, ONp=anion of β-naphthol and n=0 to 4, have been prepared by digesting pentachlorides of the metals with β-naphthol in appropriate molar ratios in carbon tetrachloride. Their structures have been elucidated from elemental analysis, conductance, magnetic susceptibility, infrared and TGA studies.

COMPARED to alkoxides, very little work has been carried out on the synthesis of metal phenoxides and naphthoxides, inspite of their utility as catalysts in many industries[1]. Prasad and coworkers[2] isolated two series of compounds of anhydrous aluminium chloride with β-naphthol. Halides of titanium(IV) and zirconium(IV) are known to react with phenols and naphthols to form the corresponding derivatives but their structural information is lacking[3]. Reaction of selenium dithiocyanate with naphthols has been found to be useful for introducing SCN group into organic compounds[4]. Naphthols have been reported to be most effective and convenient amongst the phenols for the separation of ruthenium from uranium[5]. Naphthoxides of berryllium(II) and tungsten(V) have been isolated by reacting their halides with β-naphthol[6]. It is, therefore, of interest to isolate and characterise naphthoxides of transition metals. In the present communication, we report the preparation of naphthoxides of niobium(V) and tantalum(V) and propose a possible structure on the basis of elemental analysis, molar conductance, TGA, magnetic and infrared spectral studies.

Experimental

Naphthol (A.R.) was purified by crystallisation from dry benzene. Pentachlorides of niobium and tantalum, were Fluka, analytical grade, and were used without further purification. All the organic solvents were of AnalaR grade. They were further dried by appropriate drying agents and fractionally distilled.

Compounds of composition $MCl_4(ONp)$, $MCl_3(ONp)_2$ and $MCl_2(ONp)_3$, where M stands for niobium or tantalum and ONp stands for the anion of β-naphthol, were obtained by mixing corresponding pentachlorides with β-naphthol in exact 1 : 1, 1 : 2 and 1 : 3 molar ratio in dry carbon tetrachloride and continuous stirring at room temperature till there was no evolution of HCl gas. But in case of compounds of composition $MCl(ONp)_4$ and $M(ONp)_5$, the corresponding mixture solutions were heated occasionally (not more than 60°). To ensure complete substitution by naphthoxy groups in the last compound, β-naphthol in 1 · 5 molar ratio was taken in a little excess and digested till there was no evolution of HCl gas. The compounds so obtained were filtered, washed repeatedly with dry benzene and finally dried under vacuum.

Niobium and tantalum were estimated as their pentoxides and chlorine by Volhard's method. Infrared spectra of the complexes were recorded on a double grating infrared spectrophotometer, Perkin-Elmer 337 and 621, in KBr pellets. Molar conductance values of $10^{-3}M$ solutions of these compounds in nitrobenzene were determined using a cell of cell constant 0.384 at 25±0.1° with a Toshniwal conductivity bridge, CL01/01A Sr. No. 447. Thermogravimetric analysis was carried out on a Stanton thermogravimetric balance, model AD-2 at a heating rate of 5°/min. Magnetic susceptibility measurements were made on a Guoy's balance at room temperature.

Results and Discussion

The reactions of pentachlorides of niobium and tantalum with β-naphthol in carbon tetrachloride were found to be slow but became facile on digestion. All attempts to isolate a solvate of β-naphthol with pentachlorides of niobium and tantalum at room temperature were unsuccessful, possibly because of the greater lability of the proton of naphthol. The niobium compounds gave dull orange crystals whereas the tantalum oompounds were sulphur yellow in colour. Stoichiometric composition of these compounds was established by elemental analysis and results are reported in Table 1. All these compounds are moisture sensitive and change their colour on exposure but are sufficiently stable in dry air. They are insoluble in most organic solvents except slight solubility in nitrobenzene and dimethylformamide. Molar conductance values of $10^{-3}M$ solutions in nitrobenzene (Table 1) suggest that the compounds are non-ionic

TABLE 1—ANALYTICAL DATA OF THE ISOLATED NIOBIUM AND TANTALUM COMPLEXES

Compound	Colour	Elemental analysis				Molar conductance in nitrobenzene
		%Found		%Reqd.		($ohm^{-1} cm^2 mole^{-1}$)
		M	Cl	M	Cl	
$Nb(ONp)_5$	Brick red	10.80	—	11.50	—	18*
$NbCl(ONp)_4$	Light brick red	13.00	4.95	13.82	5.07	2
$NbCl_2(ONp)_3$	Deep orange	14.28	11.25	15.70	12.00	3
$NbCl_3(ONp)_2$	Orange	18.88	21 28	19.15	21.97	2
$NbCl_4(ONp)$	Orange	25.02	36.82	24.16	37.05	16*
$Ta(ONp)_5$	Dull yellow	20.00	—	20 20	—	10*
$TaCl(ONp)_4$	Deep yellow	21.82	4.08	22 90	4.50	2
$TaCl_2(ONp)_3$	Sulphur yellow	25.89	9.72	26.60	10.40	2
$TaCl_3(ONp)_2$	Yellow	30.74	17.81	31.20	18.60	11*
$TaCl_4(ONp)$	Yellow	37.25	29.31	38.80	30.40	2

* In dimethylformamide.

in nature. Molecular weight determinations could not be carried out because the compounds are insoluble in solvents suitable for cryoscopy. They are diamagnetic, excluding thereby the possibility of any reduction of the metal to the lower oxidation state.

Infrared spectra of these compounds show a significant change in the spectrum of the pure ligand on complex formation. The broad band in the region 3360-3460 cm^{-1}, assigned to hydrogen bonded phenolic hydroxyl group in β-naphthol[7], is altogether missing in all the compounds. This indicates that there is no phenolic hydroxyl group present in these compounds, which is also supported by the observation that hydrogen chloride gas was liberated during the course of their preparation. A perusal of the spectra of these compounds suggests that the changes in various bands are similar to the ones observed for various aromatic tertiary bases upon complex formation with metal[7] and non-metal halides[8]. The sharp bands at 3052 and 3074 cm^{-1} assigned to $\nu(C-H)$ in β-naphthol are observed at the same positions in the compounds. Furthermore, the most important and strong band at 1260 cm^{-1} in pure β-naphthol[9] due to $\nu(C-O)$ stretching mode, shifts to lower spectral regions by about 40-50 cm^{-1} in the spectra of these compounds. This shift may be attributed to the drainage of electrons from the ring to the metal through C–O bond. The important bands are given in Table 2.

TABLE 2—PRINCIPAL INFRA RED BANDS (cm^{-1}) OF THE NIOBIUM(V) AND TANTALUM(V) COMPLEXES

Compound	$\nu(O-H)$	$\nu(O-C)$	$\nu(M-O)$	$\nu(M-Cl)$
NpOH	3400	1260	–	–
$Nb(ONp)_5$	—	1190	540, 580	–
$NbCl(ONp)_4$	–	1220	546, 578	349
$NbCl_2(ONp)_3$	–	1210	548, 570	352
$NbCl_3(ONp)_2$	–	1198	542, 568	348
$NbCl_4(ONp)$	–	1204	540	340
$Ta(ONp)_5$	–	1210	502, 545	–
$TaCl(ONp)_4$	–	1215	518, 548	333
$TaCl_2(ONp)_3$	–	1198	510, 550	342
$TaCl_3(ONp)_2$	–	1220	498, 552	338
$TaCl_4(ONp)$	–	1202	506	335

Metal coordination to the ligand has been further confirmed by the appearance of new bands (not present in the pure ligand) in the lower wave number region. Intense bands around 570-580 cm^{-1} in case of niobium and around 540-550 cm^{-1} in case of tantalum compounds may be assigned to ir active terminal $\nu(M-O)$ stretching modes. Such type of bands, assigned to terminal M–O bonds in the alkoxides of these metals, have also been reported earlier in the same region[10,11]. It is interesting to note that in these compounds no band around 900-930 cm^{-1}, which could be assigned to Nb=O or Ta=O stretching modes[12], has been observed suggesting that no oxygen abstraction occurs in these compounds.

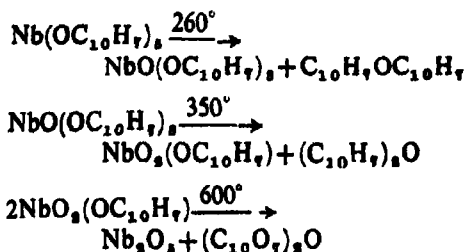
In the case of the compound of composition $NbCl_4(ONp)$, an intense and sharp band at 540 cm^{-1} has also been observed. Since this band is well below the range 570-580 cm^{-1} observed for terminal $\nu(Nb-O)$ stretching mode[11], it may be attributed to bridging $Nb \diagup^{O} \searrow Nb$ mode. This assignment is quite in agreement with earlier observations[11,13]. Furthermore, a sharp intense band at 340 cm^{-1} assigned to $\nu(Nb-Cl)$ stretching vibrations is observed which is in agreement with the assignments of Djordjevic[14] and with the reported $\nu(Nb-Cl)$ vibrations for octahedral complexes[15]. No band that could be assigned to bridging chlorine, which is expected to fall below 330 cm^{-1}[13], has been observed. Based upon ir spectral data and insolubility in various solvents, a possible dimeric structure via bridging through naphthoxy groups may be proposed. Similar observations have been made in case of tantalum compounds. These propositions also find support from previous work on the alkoxides and phenoxides of niobium and tantalum[16-18].

Thermal mode of decomposition and relative strength of bonds in these naphthoxides have been inferred from the weight changes noted from thermograms. In the case of the compound $NbCl_4(ONp)$, a molecule of chloronaphthalene is lost at ~158° leaving behind niobium oxytrichloride, which decomposes further via dioxymonochloride (NbO_2Cl) formation at ~260° followed by

subsequent disproportionation to the pentoxide and pentachloride[19] at about 600°. However, in case of fully substituted naphthoxide, i.e. $Nb(ONp)_5$, the major intermediate products are dinaphthyl ether and niobiumoxytrinaphthoxides as shown below :

$$Nb(OC_{10}H_7)_5 \xrightarrow{260^\circ} NbO(OC_{10}H_7)_3 + C_{10}H_7OC_{10}H_7$$

$$NbO(OC_{10}H_7)_3 \xrightarrow{350^\circ} NbO_2(OC_{10}H_7) + (C_{10}H_7)_2O$$

$$2NbO_2(OC_{10}H_7) \xrightarrow{600^\circ} Nb_2O_5 + (C_{10}O_7)_2O$$

The final product in all the naphthoxides has been found to be M_2O_5. Formation of these intermediates is supported by the earlier reports on the mode of decompositions of alkali metal[20] and transition metal phenoxides[21]. It can thus be concluded that these naphthoxides have sufficient thermal stability be·ause of their polymeric structure.

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Complexing Behaviour of N-Cyclo Hexyl Benzothiazole Sulphonamide with Cu(II), Mn(II), Ni(II), Co(II) and Fe(III)

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Metal complexes of the type ML_2X_2 and $M'L_2X_3$, [M = Cu(II)), Mn(II), Ni(II) or Co(II); M' = Fe(III); X = Cl^-, CH_3COO^-, NO_3^- or $C_6H_2(NO_2)_3O^-$ and L = N-cyclo hexyl benzothiazole sulphonamide] have been synthesized and characterised on the basis of elemental analysis, magnetic susceptibility measurements and spectral studies. The ligand behave as a bidentate chelating agent in all the complexes. All the complexes exhibit octahedral stereochemistry. They were screened for fungicidal activity against *Drechslera tetramera*, *Alternaria alternata* and *Fusarium oxysporum*.

THERE has been considerable interest in recent years in the study of complexes with benzothiazole, imidazole and thiazole ligands[1-4]. A perusal of literature shows that no work on transition metal complexes of N-cyclo hexyl benzothiazole sulphonamide has been carried out. We report here the preparation and characterisation of Cu(II), Mn(II), Ni(II), Co(II) and Fe(III) complexes with N-cyclo hexyl benzothiazole sulphonamide. The newly synthesized complexes were also screened against different fungi.

Material and methods : All the chemicals used were either C. P. or A. R. grade. The ligand was used after recrystallisation.

Preparation of metal complexes : An alcoholic solution of the appropriate metal salt (1 mole) was refluxed with an alcoholic solution of the ligand (2 mole) for 0.5 hr. The reaction mixture was concentrated to half its volume. Solid complex separated out on cooling which was filtered, washed successively with ethanol and ether and dried *in vacuo*.

The analysis of metal, sulphur and nitrogen were carried out by standard methods. IR spectra of the ligand and complexes were recorded on a Beckmann spectrophotometer model IR-20 in the range 4000-200 cm^{-1}. Magnetic susceptibility measurements of complexes were done by Gouy's method at room temp. using mercury tetrathiocyanato cobaltate as calibrant. The results are given in Table 1.

All the complexes and ligands were screened for their fungicidal activity using three different fungi by growth method.

Results and Discussion

On comparing the infrared spectra of the ligand with those of the complexes, it was found that the positions of most of the bands had shifted. The

TABLE 1—ELEMENTAL ANALYSIS AND MAGNETIC SUSCEPTIBILITY DATA

Complex	%N Found (Calcd.)	%S Found (Calcd.)	%M Found (Calcd.)	Magnetic susceptibility B. M.
L	9.50 (9.45)	21.50 (21 52)	—	—
$(CuL_2)(NO_3)_2$	10.88 (10.90)	16.58 (16.54)	8.20 (8.15)	1.85
$(MnL_2)(NO_3)_2$	10.91 (10.89)	16.55 (16.60)	7.08 (7 13)	6 00
$(NiL_2)(NO_3)_2$	10.86 (10 84)	16.60 (16.54)	7.52 (7.57)	3 16
$(CoL_2)(NO_3)_2$	10.88 (10 83)	16.55 (16.51)	7.58 (7.61)	4 95
$(FeL_2)(NO_3)_3$	11.17 (11.24)	16.92 (16.99)	5.00 (4.98)	5.89
$(CuL_2)(OAc)_2$	7.29 (7.28)	16.60 (16.54)	8.15 (8.21)	1.87
$(MnL_2)(OAc)_2$	7.42 (7.39)	16.75 (16.70)	7 12 (7.18)	5 87
$(NiL_2)(OAc)_2$	7 22 (7.28)	16.70 (16 65)	7.61 (7.68)	3.19
$(CoL_2)(OAc)_2$	7.31 (7 28)	16 66 (16 64)	7.65 (7 67)	4 92
$(FeL_2)(OAc)_3$	7.42 (7 40)	17.08 (17.13)	5.02 (4.97)	5 94
$(CuL_2)(Cl)_2$	7.72 (7.70)	17.66 (17.61)	8.80 (8.74)	1 86
$(MnL_2)(Cl)_2$	7.82 (7.79)	17 85 (17 82)	7.62 (7.66)	5 90
$(NiL_2)(Cl)_2$	7.77 (7.75)	17.80 (17.73)	8.11 (8 13)	3.18
$(CoL_2)(Cl)_2$	7.79 (7.75)	17.68 (17.72)	8 19 (8.17)	5.08
$(FeL_2)(Cl)_3$	7.92 (7 99)	18.32 (18.28)	5.36 (5 31)	5 99
$(CuL_2)[C_6H_2(NO_2)_3O]_2$	12.61 (12.59)	11.48 (11.51)	5.80 (5 71)	1.88
$(MnL_2)[C_6H_2(NO_2)_3O]_2$	12.55 (12.69)	11.65 (11.60)	4.90 (4.98)	5.88
$(NiL_2)[C_6H_2(NO_2)_3O]_2$	12.58 (12.65)	11.60 (11.56)	5.25 (5.30)	3.20
$(CoL_2)[C_6H_2(NO_2)_3O]_2$	12.60 (12.64)	11.54 (11.56)	5.35 (5.32)	4.98
$(FeL_2)[C_6H_2(NO_2)_3O]_3$	12.98 (12.90)	11.80 (11.78)	3.40 (3.42)	5.90

$L = C_{13}H_{16}N_2S_2O_2$

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bands for sulphonamide group observed at 1305 and 1180 cm^{-1} in the ligand were shifted to 1325-1315 and 1170-1150 cm^{-1}, respectively. νC–S observed at 640 cm^{-1} in the ligand was shifted to a position below 600 cm^{-1} in the spectra of the complexes. In all the complexes a new band appeared around 500 cm^{-1} which is assigned to M–N band. These evidences clearly show that complexation is taking place through the S of thiazole ring and N of sulphonamide group.

The asymmetric and symmetric C=O stretching frequencies of acetate ion expected at 1578 and 1425 cm^{-1}, respectively are observed around 1550-1530 and 1450-1435 cm^{-1}, respectively in acetato complexes. The changes in these modes on complexation suggest that acetate group behaves as a unidentate ligand in all the acetato complexes[5].

The magnetic moment values of the Cu(II) complexes are in the range of 1.84-1.88 B. M. The μ_{eff} values of the complexes suggest an octahedral or distorted octahedral stereochemistry[6]. All the copper complexes show an electronic spectral band in the region 13000-16000 cm^{-1} which may be assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$ characteristic of distorted octahedral Cu(II) complexes[7].

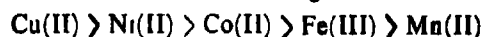
The magnetic moment values of Co(II) complexes lie in the range 4 90-5 1 B. M. which is characteristic of high spin octahedral complexes. The electronic spectra of Co(II) complexes show two absorption bands at 8870 and 20000 cm^{-1}. The first band may be identified with the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and the second band may be due to the transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. The absorption bands in the electronic spectra of Co(II) complexes are approximately similar to those reported for octahedral complexes[8-11].

The magnetic moment values of Ni(II) complexes are in the region 3.16-3.20 B. M. which show the presence of two unpaired electron. The values are typical of octahedral Ni(II) complexes. The electronic spectra of Ni(II) complexes show bands around 9300 cm^{-1}, 15750 cm^{-1} and 25974 cm^{-1}, characteristic of octahedral Ni(II) ion. These bands may be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively.

The observed magnetic moment values of Fe(III) complexes are in the region 5.88-6.00 B. M. and support the octahedral stereochemistry of Fe(III) complexes. The electronic spectra of Fe(III) complexes show a weak band around 9200 cm^{-1} assignable to $^6T_{2g} \rightarrow {}^6E_g$ which is characteristic of high spin octahedral Fe(III).

Magnetic susceptibility measurements of the Mn(II) complexes at room temp. suggest that Mn(II) complexes are high spin and display magnetic moment values in the range 5.85-6.00 B. M. expected for five unpaired electrons in a weak octahedral field. The electronic spectra of Mn(II) complexes show four bands at 19800, 23000, 29000 and 34000 cm^{-1}. These bands may be assigned to the transition $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(D)$ and $^6A_{1g} \rightarrow {}^4T_{1g}(P)$. The magnetic moment values and electronic spectra support the octahedral configuration.

Fungicidal screening : All the complexes exhibited significant fungitoxicity at 500, 200 and 100 ppm, the inhibition ranging from 60 to 88%, 31 to 60% and 24 to 35%, respectively. The toxicity of metal chelates in the descending order is as follows

Cu(II) > Ni(II) > Co(II) > Fe(III) > Mn(II)

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Synthesis and Characterization of Complexes of Co(II), Cu(II), Cd(II), Mg(II) with Disubstituted Thioureas

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N-2-(6-methyl substituted pyridyl)-N'-substituted thioureas, N-2 (5-chloro substituted pyridyl)-N'-substituted thiourea and N-α-naphthyl-N'-substituted thiourea and their Co(II), Cu(II), Cd(II) and Hg(II) complexes were synthesized and characterized by elemental analysis. (The metals were estimated by atomic absorption spectrophotometer). Molar conductance, ir, uv and magnetic measurements were made.

TRANSITION metal complexes of substituted thioureas have been studied by several workers[1-6] but no work has been reported on Co(II), Cu(II), Cd(II), Hg(II) chloride complexes of N-2-(6-methyl substituted pyridyl)-N'-substituted thioureas, N-2-(5-chloro substituted pyridyl)-N'-substituted thiourea and N-α-naphthyl-N'-substituted thiourea. The present communication reports an attempt to study the Co(II), Cu(II), Cd(II) and Hg(II) complexes of these disubstituted thioureas.

Experimental

Chemicals All chemicals used were of B. D. H. 'AnalaR', E Merck 'GR' quality. 6-Methyl-2-amino-pyridine and α-naphthyl amine used were obtained from Sigma R Chemicals and Riedel-Haen, respectively.

Apparatus : Atomic absorption studies were performed on Perkin-Elmer-306, atomic absorption spectrophotometer. Melting points were recorded in capillary melting point apparatus (Arthur H. Thomas Co.). Conductance measurements were taken on a conductivity meter (Toshniwal, India) with dipping electrode cell. IR spectra were recorded on model 577 Perkin-Elmer IR spectrophotometer in nujol mull and uv spectra on Hitachi spectrophotometer, model 139. Magnetic measurements were performed on Gouy's balance.

Synthesis of mustard oil (isothiocyanate) : Synthesis of phenyl isothiocyanate was done by the method described by Vogel[7]. Allyl isothiocyanate and methyl isothiocyanate were synthesized by similar method except that the amines used were allyl amine and methyl amine respectively in place of aniline.

Synthesis of 5-chloro-2-amino-pyridine : The compound was prepared by the method described by Shozo Shibata *et al*[6].

Synthesis of N-2-(6-methyl substituted pyridyl)-N'-substituted thioureas, N-2-(5-chloro substituted pyridyl)-N'-substituted thiourea and N-α-naphthyl-N'-substituted thiourea : Equimolar amounts of amino compounds and mustard oil (isothiocyanate) were taken in ethanol. The mixture was refluxed for about 1-2 hr. The solution was then kept in ice-cold water for some time when substituted thiourea precipitated out as fine crystals. The precipitate was filtered and washed with ethanol and finally recrystallised from ethanol and dried in a vacuum desiccator.

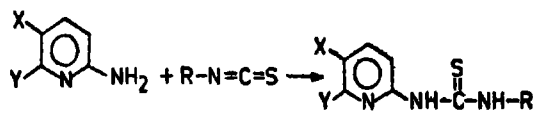
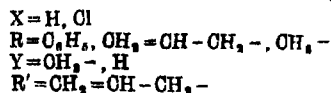
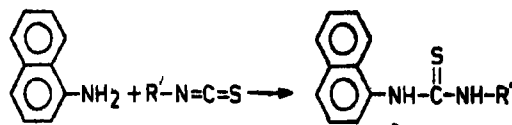
In the case of 2-amino-5-chloro-pyridine, the substituted thiourea was subjected to charcoal treatment in benzene to remove the colouring material and finally recrystallised from C_6H_6 and dried in a vacuum desiccator.

The formation of the substituted thioureas can be represented by the following equations

(X,Y-substituted 2-aminopyridine)–NH_2 + R–N=C=S ⟶ (X,Y-substituted pyridyl)–NH–C(=S)–NH–R

and

(α-naphthyl)–NH_2 + R'–N=C=S ⟶ (α-naphthyl)–NH–C(=S)–NH–R'

X = H, Cl
R = C_6H_5, $CH_2=CH-CH_2-$, CH_3-
Y = CH_3-, H
R' = $CH_2=CH-CH_2-$

Preparation of complexes . 0.01 Mole of $CoCl_2$ $6H_2O$, $CuCl_2$ $2H_2O$, $HgCl_2$ (all B D. H. "AnalaR") or $CdCl_2$ (E Merck 'GR') in *n*-butanol or ethyl alcohol was added slowly to a hot solution of 0.025 mole of the ligand in the same solvent. In the case of Co(II), the reaction mixture was refluxed for 30 to 60 min. Later, 50 to 60% solvent was evaporated. The crystallization was achieved by keeping this concentrated solution in ice-cold water for some time. Blue or bluish green crystals separated out.

Copper(II) complexes immediately precipitated out as white crystals from ethanol solution which suggests that copper(II) gets reduced to copper(I) state. In the case of mercury(II), no precipitation was obtained till the concentration ratio of metal/

ligand was raised to 1 : 1. This metal/ligand ratio resulted only in milky coloured reaction mixture which gave white crystals when kept for some time. Excess of metal chloride immediately gave white precipitate.

Cadmium(II) complexes required more vigorous condition such as metal/ligand ratio of 1 : 1 with continuous stirring in hot condition for 30-60 min followed by a precipitation time of 10-12 hr at low temperature. The complexes thus obtained were white in colour.

These complexes could not be recrystallised either from *n*-butanol or ethanol. Therefore, to ensure purity, they were washed several times with the solvent followed by 2 or 3 washings with ether (10 ml each time) and dried in vacuum.

Results and Discussion

The elemental analysis of these complexes indicates that they are formed in 1 : 2 (M : L) ratio (where L = substituted thiourea) except when N-allyl-N'-α-naphthyl thiourea is used as ligand, in which case they are in 1 : 1 (M : L) ratio. The melting points range from 152°-260° with decomposition.

The molar conductance of these complexes in DMF were found to be quite low. 1 : 1 Electrolytes generally have conductance in the range 70-110 mhos[8], showing the non-electrolytic nature of the complexes. Thus, the chlorine atoms can be considered to be coordinated to the metal ion and are not present as chloride ions. The values obtained in the present work are indicative of an octahedral geometry for these Co(II) complexes. Complexes of the other metals are diamagnetic in nature.

The uv spectra ($CHCl_3$) of these complexes exhibited two intense absorption maxima in the region of 260-280 nm and 300-310 nm, (except in the case of N-allyl-N'-α-naphthyl thiourea which showed only one thiocarbonyl π-π^* transition). These transition bands have been assigned to thiocarbonyl π-π^* and pyridyl π-π^* transitions[9,10].

All the uv spectra of the complexes were compared with uv spectra of ligands. The absorption maxima showed an erratic shift to lower or higher wave length of about 10 nm or in some cases no shift in any appreciable amount in wave length. The intensity of the absorption of complexes was higher than that of ligands. Out of the two absorption maxima, the π-π^* transition of thiocarbonyl (C=S) showed strongest interaction in metal complexes when compared with ligands.

The ir spectra of the ligands are complex and only the peaks which can be assigned with reasonable certainty are presented. From the point of view of ascertaining the donar sites of the ligands the following peaks are important: ν(C=C+C=N) (1630-1590 cm^{-1})[1-4]; r_s(NCN)+ν(NCN+C=S) (1060-1010 cm^{-1})[1-4,11] and ν(C=S) (741-722 cm^{-1})[1-4,12]. The ν(C=C+C=N) band at 1630-1590 cm^{-1} has been reported to be shifted in the case of coordinated pyridyl nitrogen[13]. The behaviour of this band is of considerable importance in deciding whether the heterocyclic nitrogen is involved in the coordination with metal. In the case of the present complexes, this band shifted to higher or lower frequencies in an irregular fashion thereby precluding any unambiguous assertion of metal ligand bonding through the pyridyl nitrogen (except for N-allyl-N'-α-naphthyl thiourea).

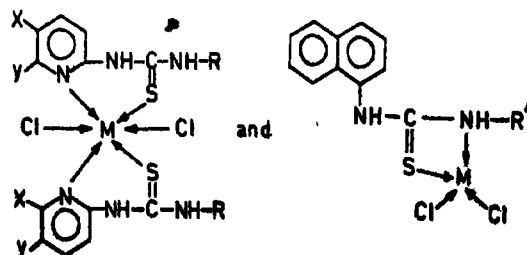
The band appearing at 1060-1010 cm^{-1} in the ligand and assigned to ν(C=C+C=S) mode, was reduced in its intensity or shifted to lower frequencies in most of the spectra of the complexes.

The mode ν(C=S), occurring at 741-722 cm^{-1}, was shifted to slight higher frequencies in metal complexes in the case of 6-methyl-pyridyl substituted thiourea ligands, while in the other complexes it was found to be reduced in intensity or shifted to lower frequencies. The shift to slight higher frequencies may be accounted for substitution effect in 6-position of pyridyl ring.

The shifting of the bands assigned to ν(NCN+C=S) and ν(C=S) mode to lower frequency (in some cases change to higher frequencies) or reduction of their intensities in metal complexes may be due to the sulphur metal coordination bond formation[1-4].

One more possible site for the coordination between metal and ligand may be one of the nitrogens of substituted thiourea unit. If this nitrogen and sulphur act as donors, a four membered chelate ring would be formed which is quite unstable in comparison to the 6-membered chelate ring formed by the donation of electrons from the nitrogen of pyridine ring and the thiocarbonyl sulphur.

From these studies of eighteen complexes of Co(II), Cu(II), Cd(II) and Hg(II), it can be reasonably concluded that complexes formed are non-electrolytes with 1 : 2 metal to ligand ratio except in the case of N-allyl-N'-α-naphthyl thiourea where the ratio is 1 : 1. The chlorine in the complexes appears to be present in the inner sphere of the complexes. On the basis of these measurements, the following structures of the complex can be assigned.

and

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Studies on Triortho-periodato Tetracobaltic(III) Acid. Part—II

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The compound $H_5[Co_4I_3O_{24}H_{12}].6H_2O$ has been prepared following two known methods – one is an alkaline method and the other is an acid method. TGA, ir and electronic spectra and powder X-ray studies have been made to throw light on its structure.

IN one of our previous communications[1], we discussed some of the properties of the interesting compound, tri*ortho*-periodatotetracobaltic(III) acid. We have now carried out thermal, spectral and powder X-ray studies of this compound. The compound has further been prepared following two known methods, the alkaline[2] and the acid methods[3]. The composition of the compound has been formulated as $H_5[Co_4I_3O_{24}H_{12}].6H_2O$. Analyses have confirmed that the composition is independent of the method of preparation. Powder X-ray study has confirmed the similarity of the crystalline nature of the compound prepared by either of the methods.

Experimental

In the alkaline method[2], the compound Na_5H_2-$Co(IO_6)_2.xH_2O$ was prepared and its saturated aqueous solution was made approximately 2*M* with $HClO_4$. This was allowed to stand for several days when a dark green crystalline solid precipitated. The crystals were dissolved in minimum amount of water and reprecipitated by making the solution 2*M* in $HClO_4$. After 2 such precipitations, the crystals were collected and analysed.

In the acid method[3], the compound, Na_3[Co(III)-$(CO_3)_3$].$3H_2O$, was prepared and dissolved in appropriate amount of $HClO_4$. A known amount of sodium metaperiodate was added to this solution. The green crystalline product obtained was collected from 2*M* $HClO_4$ as above. After 2 such precipitations the crystals were collected and analysed.

Thermal analysis: The thermograph was recorded with a Paulik-Paulik Erdey type MOM model OD-102. The derivatograph was obtained at a rate of 3°/min from room temp. to 750° using platinum crucible and samples of 150 mesh. Both DTA and DTG were recorded with the same instrument. The peaks obtained were endothermic in nature (Fig. 1). Results are shown in Table 1.

It appears from Fig. 1 that the first step of decomposition is the elimination of water molecules. The elimination takes place *via* thermally unstable intermediate ($\Delta H = 3.91$ K cal/mole). A slow phase transition has been observed in the range 270-310°. The final decomposition product is Co_3O_4.

Spectral study: Electronic spectra, both in visible and ultra violet regions, were recorded in a Hilger spectrophotometer. The results are tabulated in Table 1. The acid shows 4 bands of which 3 are in the visible to near uv region. The weak band at 22.7×10^3 cm^{-1}, which appears as a shoulder on the strong charge transfer band, is assigned to the "polynuclear band" due to a charge transfer transition[4] in the group Co<(O)(O)>Co. The first band, which appears at 16.5×10^3 cm^{-1}, agrees well with the behaviour of several $Co(O)_6$ type complexes[5] showing octahedral coordination round cobalt atoms. The band with high extinction coefficient in the near ultra violet region may also originate from charge transfer region. The maxima with high extinction coefficient in the ultra violet region is a charge transfer band characteristic of IO_6^{5-} species. From his studies on lithium *ortho*-periodate, Hauck[6] concluded that *ortho*periodates give two bands, one in the uv and the other in the near uv region. This is also in agreement with our observation.

From the energies of the visible absorption bands for the heteropoly acid, one calculates the value of the Racah parameter B to be 387 cm^{-1} (the band separation is 16B). This is very small

* For correspondence.
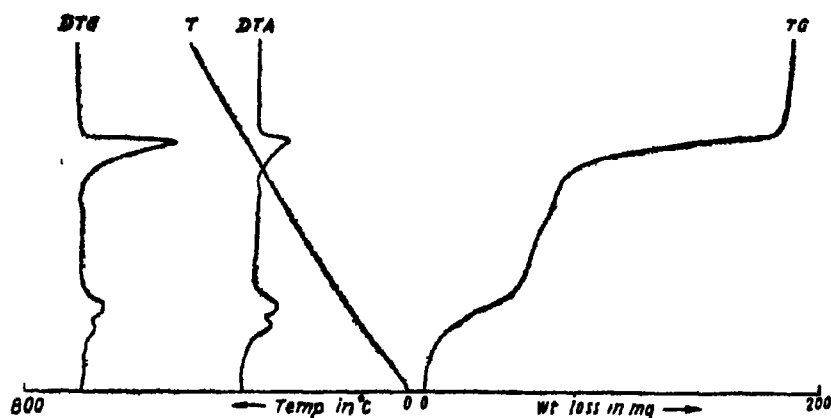
Fig. 1. Thermal decomposition of $H_3[Co_4I_3O_{24}H_{12}]\,6H_2O$.

TABLE 1—DATA OF THERMAL DECOMPOSITION AND SPECTRA
THERMAL DECOMPOSITION OF $H_3[Co_4I_3O_{24}H_{12}].6H_2O$

	Total wt. loss		Temp. °C	
	Obsd.	Calcd.	TGA	DTG (Peak temp.)
$H_3[Co_4I_3O_{24}H_{12}].6H_2O \rightarrow H_3Co_4I_3O_{24}H_{12} + 6H_2O$	110	108	50-160	140
$H_3Co_4I_3O_{24}H_{12} \rightarrow H_3Co_4I_3O_{18}$	218	216	165-215	180
$H_3Co_4I_3O_{18} \rightarrow Co_4I_3O_{15} + \frac{3}{2}H_2O + \frac{3}{2}[O]$	301.5	299	225-340	
$Co_4I_3O_{15} \rightarrow \frac{4}{3}Co_3O_4 + \frac{29}{3}[O] + \frac{3}{2}I_2$	308	303	350-500	
Co_3O_4			500-750	

Spectral Data

ν in cm^{-1}	ϵ
16.5×10^3	(410)
22.7×10^3	(425)
27.4×10^3	(2454)
44.4×10^3	(4507)

compared to the values for typical cobalt(III) complexes, 510 cm^{-1} for $[Co(H_2O)_6]^{3+}$, indicating that the interaction repulsion of the 'd' electrons is much reduced, presumably by covalency[7].

Infrared study : Infrared spectra were recorded in Perkin-Elmer model 621 and in Unicam SP 1000 Infrared spectrophotometer in CsI/Nujol phase and are shown in Fig. 2.
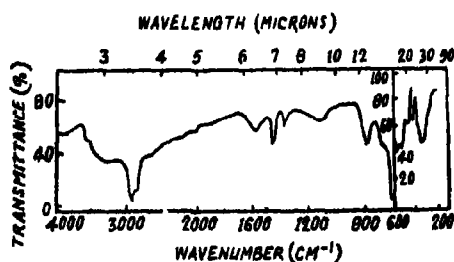
Fig. 2. Infrared spectra of $H_3[Co_4I_3O_{24}H_{12}].6H_2O$.

The broad band in the range 3600-2800 cm^{-1} is due to stretching O–H vibration. The broadening may be due to strong hydrogen bonding of the type O–H......O bridge. The bridge is comparatively short as relatively broad absorption has shifted towards lower wave number[8]. Deformation H_2O vibration has been observed at 1590-1580 cm^{-1} with the acid. Deformation –OH vibrations bonded to iodine appear as several peaks between 1300-1000 cm^{-1}, the overtones of which appear as shoulder at 2260 cm^{-1}. The band at 935 cm^{-1} may be due to coordinated water molecules. Stretching IO–(H) vibration appears at 630-670 cm^{-1} and that of IO vibration between 530 and 790 cm^{-1}. Deformation OIO vibrations appear as multiple peaks at 480-230 cm^{-1}. Co–O vibrations may be present in this region. Large number of bands in this region may be due to distortion of the octahedral IO_6 group[9-12].

X-ray powder photography : X-ray powder photography has been taken with cobalt K_α radiation in a Rigaku camera at 20°. Number of lines obtained are of little importance for any proper indexing, so that parameters of the unit cell could not be carried out by this method. The results (Table 2) show that the spacings are exactly equal for the complex periodic acid obtained from the two different methods. This indicates the similarity of their crystalline nature. Crystals of the heteropolyacid, obtained by both the methods, appear identical under microscope.

TABLE 2—POWDER X-RAY RESULTS

Compound $H_3[Co_4I_3O_{24}H_{12}].6H_2O$

Obtained by the acid method		Obtained by the alkaline method	
d in Å	Intensity	d in Å	Intensity
8.6266	m	8.6286	m
7.5322	s,b	7 5222	s,b
6.4751	m,b	6.4751	m,b
5.1920	w	5 1920	w
4.9455	s,b	4.9455	s,b
4.6213	w	4 6213	w
4.4257	w	4.4257	w
4.1654	w	4 1654	w
3.8624	w	3 8624	w
3.4881	w	3 4831	w
3.1699	vw,b	3 1699	vw,b
2.9164	vw,b	2 9164	vw,b
2 7684	vvw	2 7684	vvw
2 7008	vvw	2.7008	vvw
2.5153	s,b	2.5153	s,b
2.1421	s	2.1421	s
2 0656	w	2.0656	w
1.9927	m	1.9927	m
1.8800	w	1.8800	w
1.7367	w	1.7367	w
1 6711	vw	1.6711	vw
1 6004	vvw	1 6004	vvw
1.5657	vvw	1 5657	vvw
1.4544	vvw	1.4544	vvw
1.4268	vvw	1.4260	vvw
1.3756	vvw	1.3750	vvw

vvw = very very weak, vw = very weak, m = medium, s = strong, w = weak, b = broad.

Results and Discussions

Chemical and thermal analyses show that the complex polynuclear acids prepared by the above two methods are the same and have the general composition $H_3[Co_4I_3O_{24}H_{12}].6H_2O$, which has a formula weight of 1124. X-ray powder photography established the similarity of their crystalline nature. The compound is stable in the solid state. The aqueous solution of the compound decomposes on standing. It has been shown by potentiometric titration that the acid is tribasic with virtually identical *pk* values ($pk \sim 1.5$) and the acid equivalent is 375.

It has been observed that though the compound $H_3[Co_4I_3O_{24}H_{12}].6H_2O$ is obtained from Na_5H_2-$Co(IO_6)_2.xH_2O$ by acidification, the reverse reaction i.e. formation of the sodium salt cannot be accomplished by neutralising the above acid with NaOH, probably due to decomposition. It has also been observed that the sodium complex can be obtained by the alkaline method[8], whereas the condensed form of the complex, i.e. polynuclear acid, is obtained by the acid method[8].

Nyman and Plane[13] proposed two structures for the condensed compound, one chain and the other hexol like. The two have a notable difference in the number of water molecules, viz. 12 for the former and 6 for the latter. The latter structure is based on the Anderson model[14] where one cobalt atom takes the centre of a hexagon and the three iodine and other three cobalt atoms occupy six corners, in alternate positions, in six other hexagons. These seven octahedra are condensed by edge sharing into a flat aggregate. The compound may be formulated as $[Co\{(OH_2)_2Co(IO_6)\}_3]^{3-}$, should be optically active and be resolved into enantimorphs. Although cobalt(III) compounds are inert and optical resolution of this acid was unsuccessful, some of its derivatives, e.g. L-alanine$[Co_4I_3O_{18}$-$(OH_2)_4(L\text{-}ala)]^{4-}$, have been separated by Ama *et al*[15] into optical isomers and their O.R.D, C.D. recorded. These authors also prepared some other derivatives, e.g. $[Co_4I_3O_{18}(NH_3)_6]^{3-}$ and $[Co_4I_3$-$O_{18}(en)_3]^{3-}$, showing the complex species to contain six water molecules. Formation of 'en' complex further indicated that every two of the six water molecules take a *cis*-position to each other and this, in all probability, around each outer three cobalt atoms. All these facts suggest a hexol like structure. Our studies also reveal that the first structure of Nyman and Plane is not correct. The structure, as proposed, is not symmetric. No reason has been advanced for the different number of water molecules attached to cobalt atoms. It cannot also satisfy other experimental observations.

Electronic absorption spectra speak of the octahedral geometry round iodine and cobalt atoms. Thermal studies reveal that the twelve water molecules are linked differently to the compound in groups of six. Of these, first six molecules are lattice water, and the other six are coordinated water attached to the three outer cobalt atoms in pairs of two, that take *cis*-positions to each other. Spectral data reveal that both cobalt and iodine atoms are in octahedral environments. Racah parameter shows covalency in the solid. There is still no evidence for metal interaction in the heteropoly acid. The dark colour of the complex is due to intense electron transfer absorption in the near uv region and may also originate from distortion in the octahedral symmetry around cobalt and iodine atoms. High intensities of the electronic band may be attributed to some sort of π bonding. The intensities of the bands are high, typical of octahedral cobalt(III) complexes. Conductivity measurement[1] cannot ascertain classification of the acid to H_3A ($A = Co_4I_3O_{24}H_{12}$) type. But similar measurement on the sodium salt of the heteropoly acid, $Na_3[Co_4I_3O_{24}H_{12}].11H_2O$, has confirmed the presence of four ions (molar conductivity 330 mhos cm^2 $mole^{-1}$).

Considering all these facts, our suggestion is that the complex acid molecule possesses identical structure of $[Cr^{3+}(OH)_6Mo_6^{6+}O_{18}]^{3-}$ put forward by Perloff[16] where all cobalt and iodine atoms are octahedrally arranged by edge sharing through oxygen (Fig. 3). The periodate complexes are probably H-bonded together *via* Co-O-I attachments between adjacent complexes, as has been observed in the above Cr complexes where the Cr complexes, although weakly H-bonded together *via* waters of crystallisation, are directly attached to each other only *via* two weak Cr–O–H...OMo H bonds per

O=Oxygen
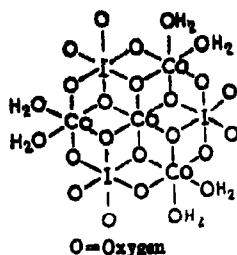
Fig. 3. Probable structure of $H_6[Co_4I_3O_{24}H_{12}].6H_2O$.

complex since the peripheral Os lack H atoms. This will give slightly elongated exterior Co–O distances. A shorter I–O distance is also presumed. Distortion from the idealised octahedral symmetry may be there due to different I–O and Co–O bond lengths. This arrangement, however, cannot explain the presence of I–OH bond, seem to be present from infrared study. NMR studies show absence of metal hydrogen bond. The compound has been shown to be monomeric from cryoscopic study in fused $Na_2SO_4.10H_2O$[17].

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Equilibrium and Formation Constants of Co(II), Ni(II) and Zn(II) Complexes of N-Benzoyl Phenyl Hydroxyl Amine in Various Mixed Aqueous Solvents

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The equilibrium constants $\beta = [ML][H]/[M][HL]$, where M = Co(II), Ni(II) or Zn(II); HL = N-benzoyl phenyl hydroxyl amine (NBPHA) and formation constant $\beta' = [ML]/[M][L]$ have been determined in five different mixed aqueous solvents namely, dioxane-water, isopropanol-water, acetone-water, ethanol-water and methanol-water in 75% v/v compositions. The order of equilibrium constants ($\log \beta_n$) are found to have no relation with $1/\epsilon$ sequence of the media, but is almost the same for different metal ions. The formation constants ($\log \beta'_n$), however, are in a sequence similar to $1/\epsilon$ sequence, with a few exceptions. In all the solvents the order of stability is Co(II) > Ni(II) < Cu(II) > Zn(II). The anomalous position of Co(II) is attributed to Jahn Teller type of distortion.

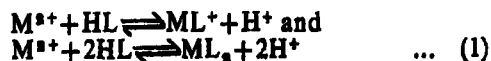
IN a previous communication[1] we reported in detail the interaction of Cu(II)-NBPHA complex system in various mixed aqueous solvents. The study has been extended to other metallic central ions e.g. Co(II), Ni(II) and Zn(II) and the findings are presented here. The physical properties of Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) complexes of NBPHA were studied and their stability constants determined in 50% v/v dioxane-water by Bag and Lahiri[2]. Shome *et al*[3] reported the stabilities of Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+} and La^{3+} complexes of NBPHA in 50% dioxane-water.

In the present work equilibrium constants for the reactions $M^{2+} + HL = ML^{+} + H$ etc., where M = Co(II), Ni(II) or Zn(II) and HL = NBPHA, and formation constants for the reaction $M^{2+} + L^{-} = ML^{+}$ etc. have been determined in five different mixed aqueous solvents in 75% v/v composition. This high volume per cent composition was maintained to cope with the solubility difficulties, considering all the solvents. The object of the present study was to investigate the solvent effects on the stability of complexes of a series of metal ions and variation of formation and equilibrium constant of a metal complex with the variation of the nature of the solvent media.

Experimental

All reagents were of A. R. or G. R. grade. The composition of the experimental solutions were described in an earlier paper[4]. The titrations were carried out in 75% v/v dioxane-water (D-W), isopropanol-water (I-W), acetone-water (A-W), ethanol-water (E-W) and methanol-water (M-W) at 30 ± 0.1°. The ionic strength was maintained constant at 0.1 *M* with $NaClO_4$. The *p*H measurements were made with a bench model Cambridge *p*H meter using glass electrodes. True [H] concentration was measured as before[4].

The equilibrium constants, β_1 and β_2, for the reactions

$$M^{2+} + HL \rightleftharpoons ML^{+} + H^{+} \text{ and}$$
$$M^{2+} + 2HL \rightleftharpoons ML_2 + 2H^{+} \quad \dots (1)$$

were calculated as reported earlier[1,4,5]. The formation constants, β'_1 and β'_2, were also calculated by the earlier reported method[1,4,5] using the relations

$$\log \beta_1 = \log \beta'_1 - \log {}^{P}K_1^H$$
$$\log \beta_2 = \log \beta'_2 - 2 \log {}^{P}K_1^H \quad (2)$$

The computation was done in BURROUGHS 6700 system as described before[4].

Results and Discussion

$\log \beta_1$, $\log \beta_2$, $\log \beta'_1$ and $\log \beta'_2$ and ${}^{P}K_1^H$ values for Co(II), Ni(II) and Zn(II) are set out in Table 1. Values of Cu(II) are taken from the previous paper[1] for comparison.

In 75% v/v solvent compositions the sequence of $1/\epsilon$ values is D-W > I-W > A-W > E-W > M-W. The values of $\log {}^{P}K_1^H$ have the sequence A-W > D-W > I-W > E-W > M-W. $\log \beta_1$, $\log \beta_2$, $\log \beta'_1$ and $\log \beta'_2$ have the following sequences for the different metal ions:

Cobalt(II):

$\log \beta_1$—E-W > I-W > M-W > D-W > A-W
$\log \beta_2$—I-W > E-W > M-W > D-W > A-W
$\log \beta'_1$—D-W > A-W > E-W > I-W > M-W
$\log \beta'_2$—D-W ≥ A-W > I-W > E-W > M-W

TABLE 1—EQUILIBRIUM AND FORMATION CONSTANTS OF Co(II), Ni(II), Zn(II) AND Cu(II) COMPLEXES OF NBPHA IN DIFFERENT MIXED AQUEOUS SOLVENTS AT 30 ± 0.1° AND 0.1M IONIC STRENGTH

Solvent composition	$1/\epsilon$	Mole fraction	*$\log {}^PK_1^H$	Metal ions	Equilibrium constants		Formation constants	
					$\log \beta_1$	$\log \beta_2$	$\log \beta'_1$	$\log \beta'_2$
75% D−W	0.0699	0.388	10.59±0.01	Co(II)	−3.29±0.002	−7.77±0.001	7.30±0.012	13.41±0.021
				Ni(II)	−3.41+0.004	−8.15+0.004	7.18+0.014	13.03+0.024
				Zn(II)	−3.03±0.002	−7.25±0.002	7.56±0.012	13.93±0.022
				*Cu(II)	−0.26±0.004	−1.58±0.004	10.33±0.014	19.60±0.024
75% I−W	0.0359	0.415	9.83±0.01	Co(II)	−3.06±0.014	−6.67±0.01	6.77±0.024	12.99±0.03
				Ni(II)	−3.08±0.011	−6.81±0.008	6.75±0.021	12.85±0.028
				Zn(II)	−2.93±0.02	−6.45±0.01	6.90±0.03	13.21±0.03
				*Cu(II)	−0.08±0.02	−1.44±0.01	9 75±0.03	18.22±0.03
75% A−W	0.0289	0.422	10.67±0.01	Co(II)	−3.51±0.006	−7.94±0.004	7.16±0.016	13.40±0.024
				Ni(II)	−3.58±0.008	−8.36±0.003	7.09±0.013	12.98±0.023
				Zn(II)	−3.46±0.015	−7.43±0.007	7.21±0.025	13.91±0.027
				*Cu(II)	−0.43±0.03	−2.00±0.02	10 24±0.04	19.34±0.04
75% E−W	0.0271	0.479	9.74±0.01	Co(II)	−2.92±0.01	−6.87±0.005	6.82±0.02	12.61±0.025
				Ni(II)	−3.02±0.007	−7.05±0.004	6.72±0.017	12.43±0.024
				Zn(II)	−2.75±0.007	−6.45±0.006	6.99±0.017	13.03±0.026
				*Cu(II)	−0.27±0.01	−1.46±0.01	9.47±0.02	18.02±0.03
75% M−W	0.0230	0.573	9.57±0.01	Co(II)	−3.18±0.007	−7.57±0.06	6.39±0.017	11.57±0.026
				Ni(II)	−3.21±0.008	−7.86±0.005	6.36±0.018	11.28±0.025
				Zn(II)	−3.12±0.006	−7.23±0.004	6 45±0.016	11.91±0.024
				*Cu(II)	−0.27±0.01	−1.62±0.01	9.30±0.03	17.52±0.03

* The values were reported earlier[1].

Nickel(II) :

$\log \beta_1$—E-W>I-W>M-W>D-W>A-W
$\log \beta_2$—I-W>E-W>M-W>D-W>A-W
$\log \beta'_1$—D-W>A-W>I-W≥E-W>M-W
$\log \beta'_2$—D-W>A-W>I-W>E-W>M-W

Zinc(II) :

$\log \beta_1$—E-W>I-W>D-W>M-W>A-W
$\log \beta_2$—E-W>I-W>M-W≥D-W>A-W
$\log \beta'_1$—D-W>A-W>E-W>I-W>M-W
$\log \beta'_2$—D-W>A-W>I-W>E-W>M-W

Copper(II) :

$\log \beta_1$—I-W>D-W=E-W=M-W>A-W
$\log \beta_2$—I-W>E-W>D-W>M-W>A-W
$\log \beta'_1$—D-W>A-W>I-W>E-W>M-W
$\log \beta'_2$—D-W>A-W>I-W>E-W>M-W

The sequence of ${}^PK_1^H$ is explained[1] as follows. Weak proton solvation of acetone puts acetone on the top. Although D-W has low dielectric constant, larger proton solvation by dioxane-water and also by the cosolvent removes dioxane from the first place to the second. The alcoholic solvents are in the sequence of their $1/\epsilon$ values. In addition, they are stronger proton solvating. That acetone water has a tendency to go higher up in the series is evident from the fact that in 75% v/v composition, although the mole fraction of A-W is a bit greater than that of D-W or I-W, it is much less than that of E-W or M-W. The difference between A-W and E-W is also very large although the difference in $1/\epsilon$ for these two compositions is quite small.

The equilibrium constants, $\log \beta_1$ and $\log \beta_2$, show random deviation from $1/\epsilon$ sequence. But one thing is remarkable. The sequences are almost unaltered by the different metal ions. Acetone-water generally has the lowest value since the cosolvent here has the least tendency to solvate proton. Alcohols go up in the sequence as they solvate protons comparatively to a larger extent.

The formation constants, $\log \beta'_1$ and $\log \beta'_2$, however have some correlation with the $1/\epsilon$ sequence in the different solvents, because proton solvation may not have here any direct influence. The order for $\log \beta'_1$ is less regular but $\log \beta'_2$ has become almost similar to the $1/\epsilon$ sequence, only that acetone-water and isopropanol-water have exchanged places. Here again, it may be noted that the nature of the metal ions has little effect on the order.

In every solvent-water system the stability sequence for metal ions is observed to be Co(II) > Ni(II) < Cu(II) > Zn(II). Co(II) is thus found to deviate from Irving and Williams' order. The entropy factor is likely to be similar in these systems. So it appears that it may be an evidence of Jahn Teller type of distortion for t_{2g}^5 set in high spin Co(II) ion ($t_{2g}^5\ e_g^2$). This may be the reason for slightly higher stability of Co(II). Higher L.F.S.E. effect of NBPHA ligand may also be a contributory factor to this.

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Stability of Complexes of Co(II), Ni(II) and Cu(II) with Esters of Salicylic Acid

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The stepwise stability constants of complexes of Co(II), Ni(II) or Cu(II) with methylsalicylate, ethylsalicylate or phenylsalicylate have been determined. The effect of temperature and ionic strength has been studied. The thermodynamic stability constants are obtained at 25°. The stability order is Cu(II) > Ni(II) > Co(II) and methylsalicylate > ethylsalicylate > phenylsalicylate. The higher values of stability constants suggest that the complexes are chelate in nature.

THE stabilities of the chelates of methylsalicylate with some metal ions of the first transition series in aqueous solutions were reported by Perrin[1]. The stabilities of ethylsalicylate complexes of Cu(II), Ni(II), Zn(II) and Hg(II) are known in literature[2]. The stabilities and thermodynamic functions of the complexes of Mn(II), Zn(II), Cd(II) and Hg(II) with esters of salicylic acid have been published from our laboratory[3,4]. A systematic study of the stabilities of the complexes of Co(II), Ni(II) or Cu(II) with methylsalicylate, ethylsalicylate or phenylsalicylate is reported in this paper.

Experimental

Bjerrum Calvin pH titration technique[5,6], as modified by Irving and Rossotti[7], has been used for investigations. The stability constants of the complexes have been determined at 25° and various ionic strengths viz. 0.05 M, 0.075 M, 0.10 M and at 35° with an ionic strength of 0.05 M in aqueous ethanol 50 : 50 (v/v). The ionic strength was adjusted by adding $NaClO_4$ solution as an inert electrolyte. In order to fulfil the condition of maximum coordination number, metal to ligand ratio was kept at 1 : 5. Since the titrations were carried out in aqueous ethanol system appropriate corrections were applied to the measurements to get the actual pH[8]. The following three solutions were titrated against a standard alkali (0.1 M KOH).

(A) 2.0 ml of 0.05 M $HClO_4$
(B) A+2.0 ml of 0.05 M ligand
(C) B+2.0 ml of 0.01 M metal ion.

The initial volume in each case was 20 ml containing aqueous ethanol system 50 : 50 (v/v). The titrations were carried at 25 ± 0.1° and 35 ± 0.1° in a constant temperature bath.

Results and Discussion

The esters of salicylic acid are weak acids due to the OH group. The values of $\bar{n}_A$, K^H_1, $\bar{n}$ and pL were calculated by the usual relationships[7]. The formation curves were obtained by plotting $\bar{n}$ against pL. The value of $\bar{n}$ does not go beyond 2 in any case for the metal complexes. This indicates the formation of 1 : 1 and 1 : 2 complexes. The

TABLE 1—STABILITY CONSTANTS OF METAL COMPLEXES OF ESTERS OF SALICYLIC ACID IN ALCOHOL : WATER SYSTEM 50 : 50 (v/v) AT 25°

Ester	Metal ion	Ionic strength M	log K_1	log K_2
Methyl salicylate	Co(II)	0.000	5.70	4.50
		0.050	4.95	3.88
		0.750	4.80	3.72
		0.100	4.70	3.62
		0.050*	5.62	4.82
	Ni(II)	0.000	6.80	4.60
		0.050	5.30	3.85
		0.075	5.20	3.75
		0.100	4.90	3.65
		0 050*	5.75	4.89
	Cu(II)	0.000	14.62	13.00
		0.050	9.37	8.50
		0.075	8.25	7.45
		0.100	7.00	6.87
		0.050*	7 43	7.00
Ethyl salicylate	Co(II)	0.000	5.60	4.40
		0.050	4.90	3.80
		0.050*	5.14	4.50
	Ni(II)	0.000	6.40	4.50
		0.050	5.16	3.82
		0.050*	5.17	4.77
	Cu(II)	0.000	8.90	8.10
		0.050	6.90	6.40
		0.050*	6.70	6.20
Phenyl salicylate	Co(II)	0.000	5.00	4.30
		0.050	4.55	3.80
		0.050*	4.60	3.87
	Ni(II)	0.000	5.60	4.40
		0.050	4.87	3.80
		0.050*	4.90	4.35
	Cu(II)	0.000	7.70	7.30
		0.050	6.55	6.05
		0 050*	6.30	5.78

* at 30°.

stability constants for the complexes were obtained by half $\bar{n}$ method and linear extrapolation method[9]. The values obtained by both the methods are in good agreement. The average values at different temperatures and ionic strengths are given in Table 1. The thermodynamic stability constants at 25° were obtained by plotting log K_n values against $\sqrt{\mu}$ and extrapolating to zero ionic strength. These are also given in Table 1.

A perusal of the values of the stability constants shows that there exists the stability order Cu(II) > Ni(II) > Co(II) with regards to the nature of the metal ions. This sequence of stability constants agrees with the Irving-Williams natural order[10] and other orders confirmed by serveral workers[11,12].

Regarding the nature of the ligands, the stability order of the complexes is methylsalicylate > ethylsalicylate > phenylsalicylate. The value of log K_1^H (the proton-ligand stability constant) has been found to decrease on increasing the bulk of the group R in $R\text{-}OOCC_6H_4OH$[8]. This explains the descending stability order of the complexes with increasing bulk of R in the esters. A comparison of the stabilities at 25° and 35° shows that the effect of rise of temperature on the stability of the complexes becomes less and less pronounced in going from methylsalicylate through ethylsalicylate to phenylsalicylate.

Another important factor influencing the stability is ionic strength of the medium. It is apparent from the stabilities at 25° with different ionic strengths (Table 1); the stabilities record a decrease with an increase of ionic strength. This is in accordance with the earlier conclusions of Debye[13]. In media of higher ionic strength the metal ions are shielded from the ligands by the other ions present. This results in low rates of combination of the metal ions with the ligands.

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Spectrophotometric Determination of Dissociation Constants of Violuric Acid and Stability Constant of its Cu(II) Complex

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Spectrophotometric studies of Cu(II)-violuric acid system indicate the presence of 1 : 2 complex in the pH range 4.0-6.5. The apparent equilibrium constant (K_1^c) has been determined by general absorbance-extinction-concentration scheme. The thermodynamic values of the first and second dissociation constants of the ligand have been determined while the third dissociation constant has been determined at I=1.0. The effects of pH stress and buffer compositions on the dissociations have also been investigated. The stability constant of the complex is found to be 14.60 at pH 5.5 and I=0.10.

THE coordinative interactions of substituted barbituric moieties are of great importance in elucidating various enzymatic and drug actions. Isonitroso barbituric acid or violuric acid forms chelates with different metal ions[1-4]. Apart from this analytical potentiality, no systematic work has been done on this acid and as such it was decided to make a thorough study of its chelation to Cu(II). As a knowledge of dissociation constants of the acid is required, these have also been determined by spectrophotometric technique.

Experimental

Violuric acid (VA) of E. Merck chromatographic grade was used without further purification. Carbonate-free NaOH and $HClO_4$ (A. R., E. Merck) solutions were used for adjusting the pH to the desired value. Other chemicals used were of AnalaR grade. All studies were made in conductivity water.

The pH was measured with an ELICO-pH meter (India) fitted with glass and saturated calomel electrodes. The uv absorption spectra of VA at various pH values were recorded on Carl-Zeiss Specord recording spectrophotometer. The visible spectra of the complex were measured with Bausch and Lomb Spectronic-20. All absorbance measurements were taken with 1 cm cells at room temperature (25 ± 0.5°).

For studies of dissociation, a solution of 2.0×10^{-5} M violuric acid at an ionic strength of 0.10 was used; some measurements were taken at variable ionic strength ranging from 0.02 to 0.35. For determining pK_3, the ionic strength had to be maintained, of necessity, at 1.0. For studies on the Cu(II) complex, concentrations were varied at a fixed M/L (1 : 2) ratio and constant ionic strength (0.10).

Results and Discussions

The spectra of violuric acid (VA) in solution strongly depend on the pH of the media indicating successive deprotonation equilibria. The significant bands of VA are at 252 nm in strongly acid solution (pH 1.25) and at 220 nm and 312 nm in the alkaline medium (pH 8.0). Beyond pH 10.0, the absorption occurs at 325 nm with an isosbestic point at 318 nm. In a more basic medium (pH 13.50), the characteristic peak is at 310 nm. Interpreting the spectral behaviour in terms of three successive dissociation equilibria, the molecular acid H_3L would correspond to pH 2.50, the monoanion, H_2L^-, would be present around a pH 8.0 and the dianion, HL^{2-}, at about a pH of 12, respectively. To identify fully ionized VA i.e., L^{3-}, the spectrum of VA in 2 M NaOH was recorded and a graphical estimation[5] was also made. The extinction values obtained by the two methods agreed well.

The dissociation constants, Kc, have been calculated by the equations reported in the literature[6]. The Kc_1 and Kc_2 values were determined at several ionic strengths. The thermodynamic pK_1 and pK_2 values were determined by extrapolation method. The average values of the stepwise dissociation constants determined at several analytical wave lengths[5] are $Kc_1 = 5.88 \times 10^{-5}$(I=0.10), $Kc_2 = 1.38 \times 10^{-10}$(I=0.10) and $Kc_3 = 2.81 \times 10^{-14}$ (I=1.0).

Determination of the stability constant of Cu(II)-VA complex : In presence of a large excess of Cu(II) ions, VA shows maximum absorbance at λ=420 nm in the pH range 4.2 to 6.5. For solutions above pH 7.0, the absorption maximum shifts towards shorter wavelength and an isosbestic point is observed at 412 nm. This indicates that only one complex is formed between pH 4.2 and 6.5 but formation of more than one complex may be

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involved at pH above 6.5. The 1 : 2 composition of the complex was determined by Job's method[7].

The reaction scheme

$$Cu^{2+} + 2H_2L^- \rightleftharpoons Cu(HL)_2^{2-} + 2H^+ \quad (1)$$

is proposed to represent the interactions of Cu^{2+} ions added to a solution of VA in the pH range 4.5 to 6.5. At constant pH the apparent equilibrium constant K_1^1 is then given by

$$K_1^1 = \frac{[Cu(HL)_2]}{\{M^\circ - [Cu(HL)_2]\}\{L^\circ - [Cu(HL)_2]\}^2} \cdots (2)$$

where M° and L° are analytical concentrations of metal ion and ligand, respectively.

The stability constant (concentration quotient) of 1 : 2 complex is defined as

$$K_1 = K_1^1 \phi \quad \cdots (3)$$

where $\phi = \left[1 + \frac{[H]}{Kc_2} + \frac{[H]^2}{Kc_2 Kc_1}\right]$, and

Kc_1 and Kc_2 are the first and second concentration dissociation constants of VA. Knowing K_1^1 and ϕ at a definite pH, the stability constant of the complex can be calculated from equation 3. As the Cu(II) ion and VA do not absorb in the region of $\lambda_{max} = 420$ nm of the complex, the extinction coefficient (ϵ) of the complex is found to be 0.28×10^4 at pH 5.50 ± 0.05 and $I = 0.1$ M. The apparent equilibrium constant, K_1^1, determined by general absorbance extinction concentration scheme and the stability constant, K_1, calculated from equation 3 are $\log K_1^1 = 7.15$ and $\log K_1 = 14.60$, respectively at pH 5.50 ± 0.05 and $I = 0.1$ M.

The effect of pH on the apparent equilibrium constant, K_1^1, of the complex has been studied. The K_1^1 values were found to show no appreciable change in the pH range 4.2-6.5. A sudden lowering of the K_1^1 values above pH 7.0 may be due to the hydrolysis of unreacted Cu(II) ions and/or formation of other species. A linear plot of $\log K_1$ versus pH with slope of 1.0 suggests that the dissociation of the second proton from VA, occurring in this pH range, accompanies the association of the dianion with Cu(II) ion. This is an evidence adduced in favour of the reaction scheme (1).

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Molecular Complexes of Tetracycline and Oxytetracycline Drugs with Nucleic Acid Bases and Aromatic Amino Acids

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Spectral studies are made on tetracycline and oxytetracycline drugs with purines, pyrimidines and amino acids. $h\nu_{max}$ vs HFMO (highest filled π-molecular orbital) plots give different stabilization energies for purines, pyrimidines and amino acids. Oxytetracycline gives stronger complexes with purines, pyrimidines and amino acids than the tetracycline. The thermodynamic functions, $\Delta G°$, $\Delta H°$ and $\Delta S°$, have been calculated from the spectral data. Reasonable linear relationships have been found between $\Delta H°$ and $\Delta S°$ or $\Delta G°$ and $\Delta H°$ for these systems. The contribution of the dative bond wave function has been calculated for each complex in the ground state indicating the formation of charge-transfer complex of the order of 6-14%.

THE action of antibiotics[1] upon microorganisms may be either bacteriostatic or bactericidal. The mechanism through which the antibiotics act upon microorganisms is not fully clear. It is generally believed that the bacteriostatic effects arise from the interaction of antibiotics with bacterial enzymes, while the bactericidal effects originate in the interaction of antibiotics with cell nuclei. Molecular biologists have theorized that this interaction is due to complex formation between antibiotics and proteins on one hand and nucleic acids on the other, thereby suppressing the normal biological activity of proteins and nucleic acids. Some experimental support for this theory can be provided if the existence of molecular complexes of antibiotics with nucleic acids could be demonstrated by physical measurements. With this object in view systems containing antibiotics tetracycline and oxytetracycline, with purines, pyrimidines and amino acids in dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF) were studied and the results are reported here. Similar studies were made in water, ethylene glycol and propylene glycol where the interaction was shown to be of charge-transfer type[2].

Since tetracycline and oxytetracycline have intense absorption bands in the near ultraviolet region at 363 nm and 365 nm, respectively optical methods may be used conveniently for the study of molecular complexes in these systems. We have used four aromatic amino acids phenyl alanine tryptophan, tyrosine and histidine ; four purines adenine, guanine, xanthine and hypoxanthine and three pyrimidines cytosine, thymine and uracil in the present investigation.

Experimental

All the purines, pyrimidines and amino acids used are products of E. Merck, Darmstadt, B. D. H., England and Loba Chemical, Austria. They were of A. R. grade and used without further purification. The solvents used were of E. Merck quality. They were carefully dried and freshly distilled just before the experiments. Since traces of moisture in the solvents give completely erratic results, particular care was taken about the purification of the solvents. Tetracycline and oxytetracycline were obtained from Sigma Company, St. Louis, U. S. A. and used directly without further purification.

All spectral data were taken in Beckman model DU spectrophotometer provided with a thermostatic arrangement, using matched pairs of stoppered silica cells. Measurements with strongly absorbing systems were made in 1 cm cells whereas 10 cm cells were used when the intensity of absorption was low. Measurements were made at four different temperatures namely 23, 40, 50 and 60°. The thermostatic arrangements were kept under such control that the variation of temperature did not exceed $\pm$ 1°.

The concentrations of the donors were 10^{-2} mole/litre and those of drugs were 10^{-5} mole/litre.

Results and Discussions

The absorption spectra of tetracycline and adenine-tetracycline mixture in DMSO is given in Fig. 1. The tetracycline shows a peak at 363 nm, while adenine-tetracycline mixture shows two peaks at 363 nm and 376 nm. Adenine itself, in DMSO, has no absorption band in this region. As the adenine concentration is increased at a fixed tetracycline concentration, the optical density of the band at 376 nm increases and that at 363 nm diminishes. Evidently, the band at 376 nm arises from a molecular complex between tetracycline and adenine. When balanced against the same concentration of tetracycline in DMSO the band appears at 385 nm, definitely establishing a red shift in the spectra with respect to tetracycline band (Fig. 2).

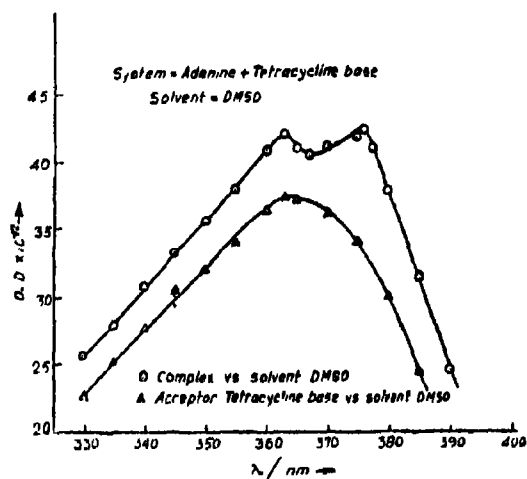



Fig. 1

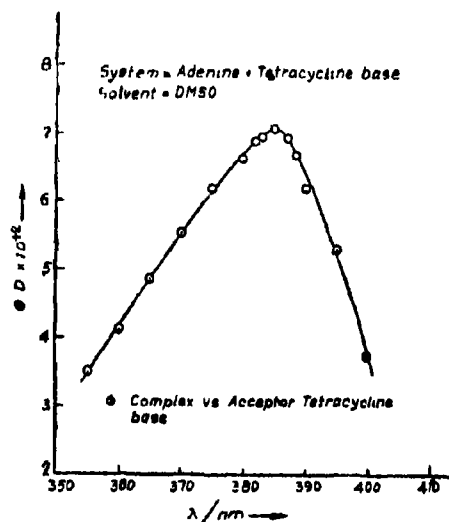



Fig 2

Similar measurements were made with other purines, pyrimidines and amino acids and new bands were detected in all the cases. Oxytetracycline behaved in a similar fashion. The relevant data are summarised in Tables 1 and 2.

The spectral measurements at a fixed concentration of antibiotic but different concentrations of purines, pyrimidines and amino acids may be utilised to determine the equilibrium constant for complex formation. Since free antibiotic absorb quite strongly at the complex band, the simple Benesi-Hildebrand[3] treatment cannot be used in the present case. For these types of situation de Maine[4] has worked out an iterative method for estimating equilibrium constants, K_c, from optical density measurements at complex band. About four/five iterations were necessary to get self consistency in K_c values. The calculated values are also given in Tables 1 and 2. A perfect linearity of $[A]/(O.D.)_c$ versus $1/[D]$ plots, where [A] is the concentration of antibiotic and [D] the concentration of donors, shows that the complexes studied are of 1 : 1 type.

The thermodynamic functions $\Delta H°$, $\Delta S°$ and $\Delta G°$ connected with the complex formation are calculated from the changes in formation constant with temperature by Van't Hoff equation (Tables 1 and 2).

It appears from the K_c values recorded in Tables 1 and 2 that antibiotics tetracycline and oxytetracycline form strong complexes with purines, pyrimidines and aromatic amino acids. So, both proteins and nucleic acid bases form strong complexes with these antibiotics. From the points of view of drug action, as stated earlier, these findings obviously mean that tetracycline and oxytetracycline will have both bactericidal and bacteriostatic effects. As a matter of fact, Snell and Cheng[5] reported that tetracyclines are bacteriostatic at low concentrations but bactericidal at higher concentrations; they decrease protein synthesis at low concentrations and nucleic acid formation at higher concentrations. It is also evident (Tables 1 and 2) that oxytetracycline forms much stronger complexes with purines, pyrimidines and amino acids than those formed by tetracycline. This may account for the selectivity of oxytetracycline as compared to tetracycline, although they have similar biological behaviour.

It must be stated categorically that this is no one-to-one correlation between the actual biological reactions and the systems studied in the present investigation. This is only a good model system reproducing reasonably well some of the findings in biological system.

Now a word about the nature of the forces involved in molecular complex formation. Since the appearance of the famous book on molecular biology by Szent-Györgyi[6], a majority of workers support the proposition that the interaction in many biological processes is charge-transfer in nature. So the question is whether the molecular complexes studied in the present case can be considered as charge-transfer complexes.

One way of verifying this is to plot $h\nu_{transition}$ against the ionization energies of the purines, pyrimidines and amino acids, considering the antibiotics as acceptors. The experimental ionization energies of all the purines, pyrimidines and amino acids are not available in the literature. However, we can take the energy of the highest filled π-molecular orbital, HFMO/β, which is related to the ionization energies of the respective compounds as calculated by Pullman and Pullman[7]. Such curves are shown in Fig. 3. The relevant data are given in Table 3. It may be observed that the plot is fairly linear for purine-, pyrimidine-tetracycline systems and for amino acid-tetracycline system. The same is true for the oxytetracycline acceptor as is evident from Fig. 4.

TABLE 1—SOLVENT DMSO

Donors	CT* λ_{max} nm Tetra-cycline	CT* λ_{max} nm Oxytetra-cycline	$-\Delta H^\circ$ K Joule mole^{-1} Tetra-cycline	$-\Delta H^\circ$ K Joule mole^{-1} Oxytetra-cycline	$-\Delta S^\circ$ Joule mole^{-1}deg^{-1} Tetra-cycline	$-\Delta S^\circ$ Joule mole^{-1}deg^{-1} Oxytetra-cycline	$-\Delta G^\circ$ K Joule mole^{-1} Tetra-cycline	$-\Delta G^\circ$ K Joule mole^{-1} Oxytetra-cycline	Temp °C	K_c L mole^{-1} Tetra-cycline	K_c L mole^{-1} Oxytetra-cycline	ϵ_c L mole^{-1}cm^{-1} Tetra-cycline	ϵ_c L mole^{-1}cm^{-1} Oxytetra-cycline
Adenine	385	388	25.11±0.28	26.58±0.15	9.54±0.08	4.19±0.04	22.26±0.06	25.32±0.02	23	70±2	120±5	14,290±635	15,088+13
									40	28.2	32.64	14,218	14,706
									50	16.23	21.84	14,164	14,652
									60	7.15	16.44	14,134	14,599
Guanine	387	389	26.32±0.18	27.33±0.17	10.71±0.09	5.73±0.02	23.10±0.04	23.61±0.03	23	59.5±1.3	81±1.4	11,770±70	12,345±50
									40	17.8	47.9	10,471	12,195
									50	9.56	23.1	10,454	12,121
									60	3.85	13.2	10,444	12,114
Hypoxanthine	392	390	22.52±0.19	23.94±0.18	7.66±0.04	3.05±0.03	20.21±0.08	23.02±0.04	23	96	105±2	12,500±64	13,384±45
									40	8.4	37.34	12,437	12,821
									50	3.4	31.6	12,422	12,656
									60	2.4	19.2	12,383	12,440
Xanthine**	397	404	28.12±0.19	26.32±0.10	14.52±0.27	9.54±0.07	23.81±0.06	23.48±0.05	23	54±0.05	93.8±0.80	17,021±103	19,193±67
									40	36.8	40.2	16,667	18,181
									50	24.2	31.08	16,528	18,018
									60	12.15	15.68	14,460	17,857
Thymine	370	371	19.13±0.09	21.26±0.08	6.48±0.04	3.67±0.08	17.20±0.05	18.79±0.06	23	16±0.05	55±1	18,100±190	20,000±145
									40	9.04	31.5	17,699	19,048
									50	5.66	21.02	17,667	19,029
									60	3.42	10.51	17,543	19,026
Uracil	371	375	23.94±0.14	25.53±0.09	8.03±0.09	3.43±0.05	21.51±0.07	24.48±0.05	23	119±1	130±0.5	13,333±955	15,385±95
									40	25.67	36.48	13,245	15,387
									50	21.15	24.40	13,236	15,326
									60	15.65	15.3	13,218	15,267
Phenylalanine	400	398	23.94±0.19	25.54±0.04	5.73±0.03	6.48±0.06	22.32±0.09	23.56±0.07	23	110±0.4	120±1	13,245±75	13,333±152
									40	30.4	45.3	13,158	13,245
									50	19.12	24.2	12,821	13,228
									60	10	12.24	12,500	13,072
Tyrosine	402	400	24.78±0.16	37.33±0.07	6.34±0.07	7.66±0.05	22.73±0.03	25.07±0.02	23	61.2±1.2	70.4±2.4	11,770±156	12,500±353
									40	35.34	46.88	11,110	12,422
									50	18.11	31.84	11,050	12,414
									60	9.0	16.13	11,019	12,399
Histidine	403	401	21.26±0.12	25.52±0.08	3.60±0.09	3.80±0.06	20.17±0.05	21.34±0.07	23	49.5±2.25	81±1.66	9,999±1304	12,384±95
									40	32.64	36	9,804	11,111
									50	12.48	18.4	9,615	10,870
									60	8.4	7.4	9,524	10,811
Tryptophan	405	402	24.32±0.17	21.26±0.04	1.88±0.07	3.43±0.04	19.54±0.09	20.21±0.09	23	36.3±1.7	40±1	16,529±246	18,181±95
									40	26	22.2	15,385	18,018
									50	20.9	13.34	15,267	17,857
									60	11.1	9.15	15,256	17,794

* Calculated from absorption data of 4 different [Donors]+[Tetracycline] or [Oxytetracycline] solutions in DMSO [Tetracycline] or [Oxytetracycline]=1.0–1.85 × 10^{-5} mole/l, [Donors] varied from 0.0435 to 0.095 moles/l using 1 cm cells.

** Xanthine using 10 cm cells.

TABLE 2—SOLVENT DMF

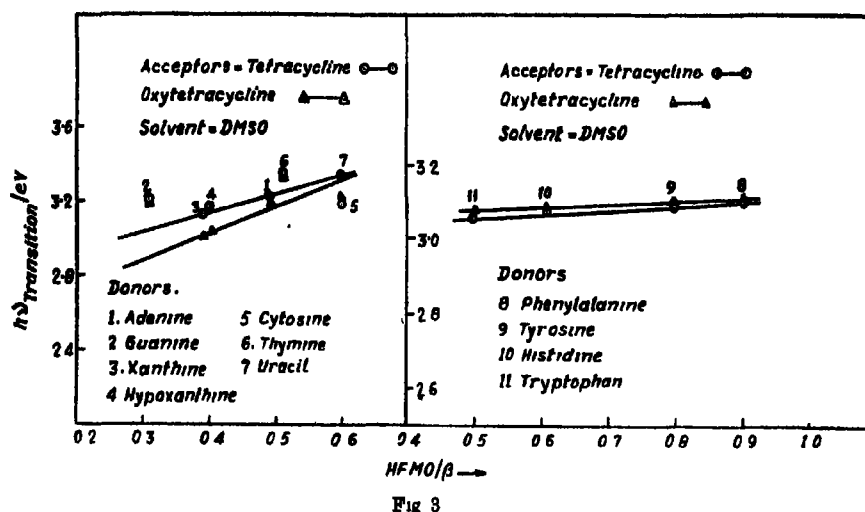
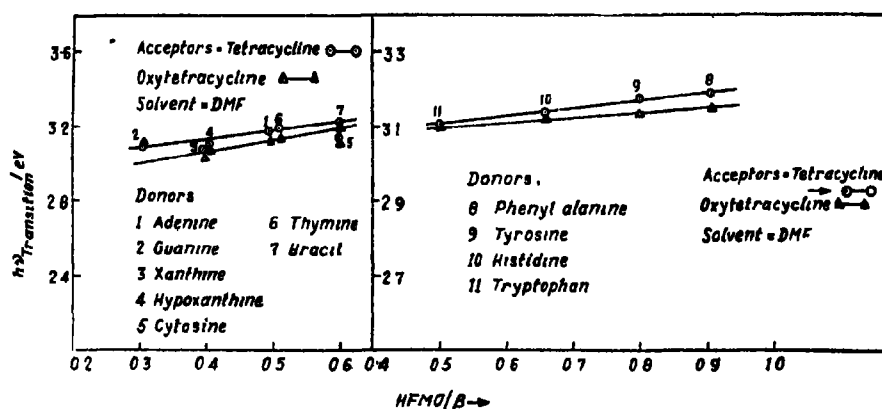
Donors	CT* λ_{max} nm Tetra-cycline	Oxytetra-cycline	$-\Delta H°$ K Joule mole^{-1} Tetra-cycline	Oxytetra-cycline	$-\Delta S°$ Joule mole^{-1}deg^{-1} Tetra-cycline	Oxytetra-cycline	$-\Delta G°$ K Joule mole^{-1} Tetra-cycline	Oxytetra-cycline	Temp. °C	K_c L mole^{-1} Tetra-cycline	Oxytetra-cycline	ϵ_c L mole^{-1}cm^{-1} Tetra-cycline	Oxytetra-cycline
Adenine	390	396	40.22±0.28	32.99±0.34	3.85±0.09	18.75±0.09	37.08±0.04	26.79±0.06	23	39.6±1	47.5±0.75	13,333±182	14,705±520
									40	16	11.2	12,500	14,285
									50	12.80	5.64	12,422	14,184
									60	6.44	3.32	12,414	14,174
Guanine	400	400	38.30±0.46	29.46±0.26	4.01±0.05	13.03±0.09	39.09±0.02	24.06±0.05	23	30±0.5	40±1	10,000±82	11,111±125
									40	16.8	19	9,523	10,989
									50	10.55	7.26	9,478	10,964
									60	7	3.65	9,488	10,958
Hypoxanthine	400	403	31.89±0.55	27.33±0.09	3.43±0.09	17.30±0.05	30.99±0.07	22.89±0.07	23	28±0.60	40.3±0.30	12,821±890	12,422±45
									40	16.4	14	12,195	11,764
									50	10	7	12,121	11,695
									60	7.2	5	12,084	11,697
Xanthine**	402	406	23.35±0.18	25.11±0.01	15.69±0.69	9.53±0.02	13.66±0.08	22.26±0.08	23	27.2±0.08	42.94±0.94	15,384±50	17,700±25
									40	20.86	35.2	15,253	16,667
									50	8	28.86	15,151	16,529
									60	3.6	13.42	15,050	16,502
Thymine	388	395	33.34±0.44	29.46±0.21	3.60±0.18	16.07±0.09	37.21±0.07	24.65±0.05	23	41.8±1.4	44±1	10,526±950	13,698±101
									40	18	15	10,000	13,333
									50	12.24	10.57	9,806	13,245
									60	8.2	4.56	9,756	13,157
Uracil	384	385	34.82±0.69	28.12±0.19	3.64±0.09	19.33±0.04	33.73±0.03	23.52±0.06	23	28.08±0.28	37.5±0.5	13,423±80	13,333±300
									40	18	16	13,333	12,500
									50	7.6	8	13,245	12,422
									60	3.4	5	12,987	12,414
Phenylalanine	390	393	32.36±0.27	29.46±0.21	14.56±0.14	16.11±0.09	23.46±0.05	24.65±0.07	23	172.5±0.5	180±4	12,820±50	13,333±19
									40	28	20.5	12,500	13,245
									50	20	8.24	12,422	13,236
									60	8	4.16	12,414	13,201
Tyrosine	392	395	34.49±0.24	30.97±0.07	16.49±0.09	17.20±0.07	33.23±0.02	25.78±0.08	23	147±3	162±3.5	9,091±125	11,111±25
									40	40	21.6	9,090	11,110
									50	15.7	11	8,695	11,049
									60	5	4.34	8,658	11,043
Histidine	395	396	27.33±0.19	27.33±0.19	12.22±0.13	14.52±0.05	26.07±0.04	23.02±0.04	23	98±2	126±1	10,204	12,048±45
									40	32	15.3	10,152	11,764
									50	14	10.26	10,147	11,695
									60	7	3.44	10,141	11,689
Tryptophan	400	399	23.94±0.18	26.37±0.04	11.46±0.06	13.81±0.03	20.51±0.05	22.22±0.06	23	161±1	173±0.54	11,765±62	12,500±55
									40	24.6	29.4	11,049	12,422
									50	12.67	12.66	11,043	12,414
									60	3.68	8.48	11,019	12,407

* Calculated from absorption data of 4 different [Donors]+[Tetracycline] or [Oxytetracycline] solutions in DMF, [Tetracycline] or [Oxytetracycline] $= 1.0 - 1.85 \times 10^{-3}$ mole/l ; [Donors] varied from 0.0435 to 0.095 mole/l using 1 cm cells.

** Xanthine using 10 cm cells.

Fig 3

Fig. 4

TABLE 3

Donors	Solvent DMSO $\bar{\nu} \times 10^{-3}$ (cm^{-1})		Solvent DMF $\bar{\nu} \times 10^{-3}$ (cm^{-1})		HFMO (β)
	Tetra-cycline	Oxytetra-cycline	Tetra-cycline	Oxytetra-cycline	
Adenine	25.97	25.77	25 64	25.25	0.486
Guanine	25.84	25.71	25.00	25.00	0.307
Xanthine	25.19	24.75	24.87	24 63	0 397
Hypoxanthine	25.51	25.64	25.00	24.81	0.402
Cytosine	25.64	25.84	25.31	25 12	0 595
Thymine	27.08	26.95	25.77	25.31	0 510
Uracil	26.95	26.67	26.04	25.97	0 597
Phenylalanine	25.00	25.18	25.64	25.44	0 908
Tyrosine	24.88	25.00	25.51	25.31	0.792
Histidine	24.81	24.94	25.81	25.25	0.660
Tryptophan	24.69	24.87	25.00	25.06	0.534

The reason for the two different plots for the two systems is obvious. The energy of charge-transfer transition is given as

$$h\nu_{CT} = I_D - E_A - \Delta.$$

where I_D is the ionization energy of the donor, E_A the electron affinity of the acceptor and Δ is the stabilization energy of the donor-acceptor pair. The linear $h\nu_{transition}$ vs HFMO plot indicates a constant value for Δ. This may be true for chemically allied donors but is not certainly valid for completely chemically dissimilar donors like purines, pyrimidines and amino acids.

We may conclude that linear $h\nu_{transition}$ vs HFMO plots indicate that the purines, pyrimidines and amino acids are acting as donors and tetracycline and oxytetracycline as acceptors in the molecular complexes in two solvents and the complex is of charge-transfer type.

Regarding the temperature variation, we may observe that the formation constants, K_c, and the extinction coefficient, ϵ_c, both diminish with rise of temperature. In Figs. 5, 6, 7 and 8 plots of $-\Delta S°$ vs $-\Delta H°$ and $\Delta G°$ vs $-\Delta H°$ are shown. These are found to be fairly linear as reported earlier[8]. The position of equilibrium showed reversibility with temperature. The negative enthalpy term and the intensification of band on cooling clearly indicate the charge-transfer nature of the complex[9].

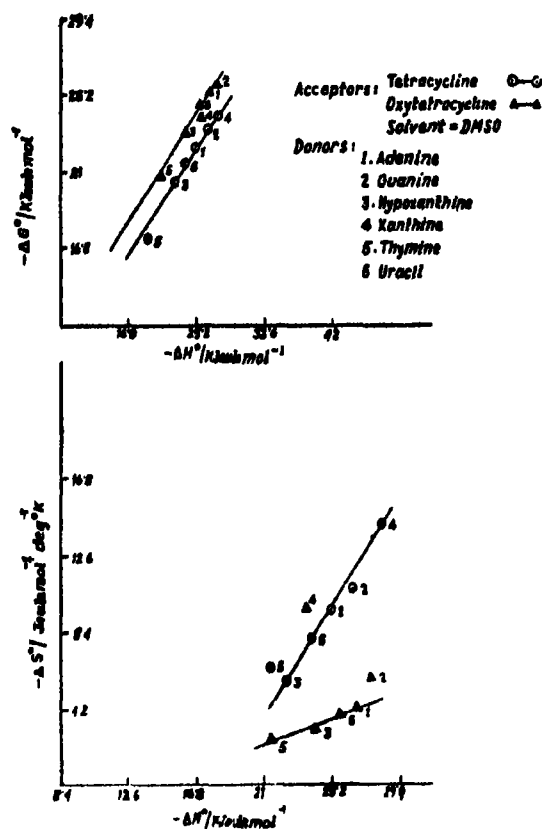
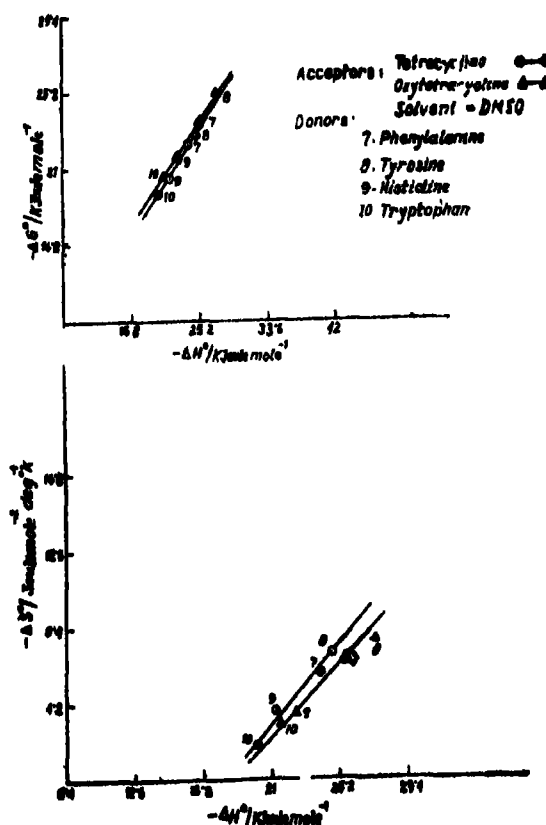



Fig. 5

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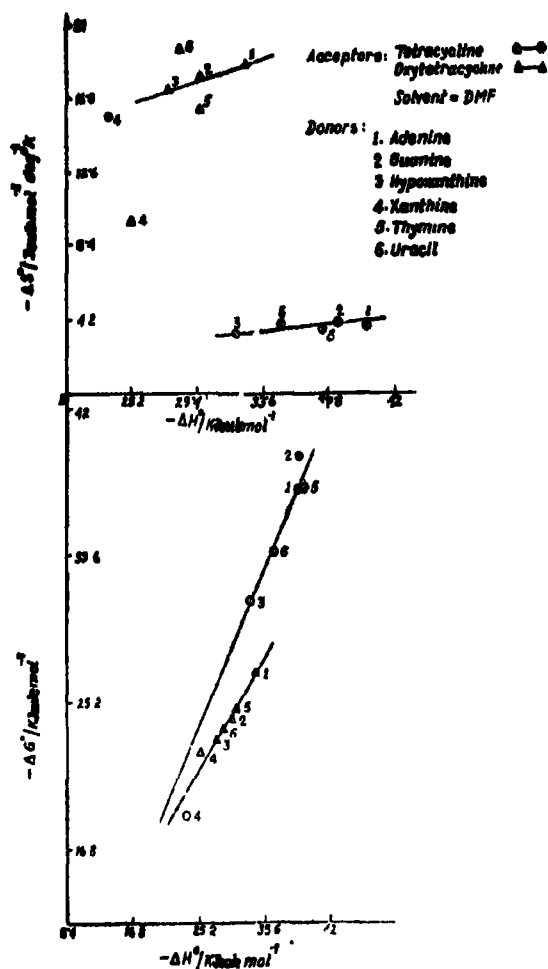


Fig. 7

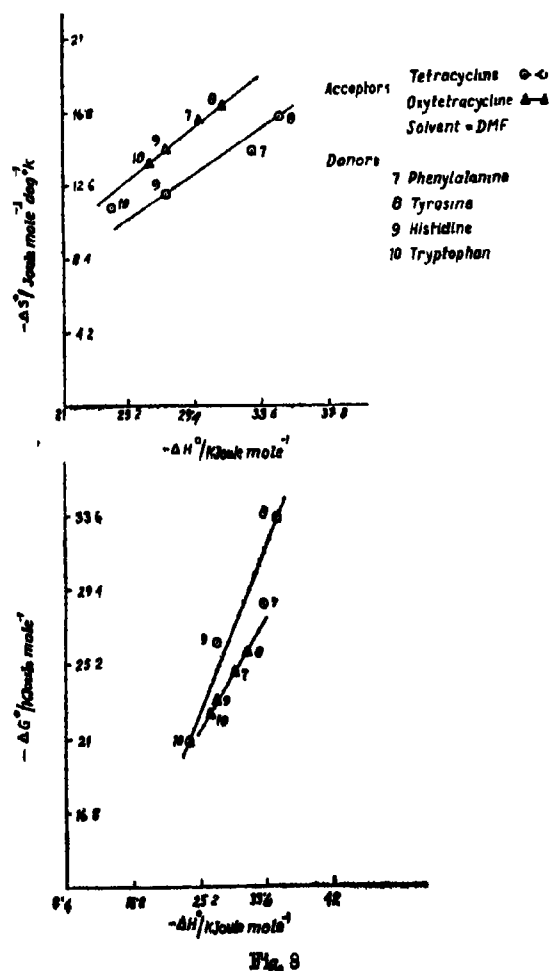
As is observed, the formation constants increase with increase[10-13] in dielectric constant of the medium for the purines and pyrimidines whereas these decrease[14] with increase in the dielectric constant of the medium for the amino acids. Since charge transfer complexation takes place on a molecular level, the formation constant may be expected to be independent of the bulk dielectric constant. If the electrostatic interaction holds the molecules together, the formation constant will depend strongly on the dielectric constant of the medium and in fact will be lowered with an increase in the dielectric constant of the medium[14]. However, considering the various factors contributing to the formation of charge-transfer complexes, it is practically difficult to separate the influence of one factor from the others. Moreover, the high dielectric constants of the solvents used should have a direct impact also. As previously[15] pointed out, the model developed from the concept of reaction field[16], though capable of describing approximately the interaction between a solute and weakly polar solvents, becomes too crude an approximation for polar solvent.

TABLE 4—SOLVENT DMSO : ESTIMATED CONTRIBUTION OF THE DATIVE BOND WAVE FUNCTION FOR PURINES, PYRIMIDINES AND AMINO ACIDS+TETRACYCLINE/OXYTETRACYCLINE

Donors	$-\Delta H^\circ$ (ev)		$h\nu_{CT}$ (ev)		b^2/a^2	
	Tetracycline	Oxytetracycline	Tetracycline	Oxytetracycline	Tetracycline	Oxytetracycline
Adenine	0.26	0.27	3.22	3.20	0.0807	0.0861
Guanine	0.27	0.28	3.20	3.19	0.0850	0.0888
Hypoxanthine	0.23	0.27	3.17	3.07	0.0737	0.0888
Xanthine	0.29	0.25	3.18	3.18	0.0932	0.0779
Thymine	0.20	0.26	3.38	3.34	0.0594	0.0825
Uracil	0.25	0.22	3.34	3.31	0.0741	0.0659
Phenylalanine	0.25	0.26	3.10	3.12	0.0799	0.0848
Tyrosine	0.26	0.28	3.09	3.10	0.0832	0.0918
Histidine	0.22	0.23	3.08	3.09	0.0715	0.0754
Tryptophan	0.21	0.22	3.06	3.08	0.0681	0.0714

TABLE 5—SOLVENT DMF : ESTIMATED CONTRIBUTION OF THE DATIVE BOND WAVE FUNCTION FOR PURINES, PYRIMIDINES AND AMINO ACIDS+TETRACYCLINE/OXYTETRACYCLINE

Donors	$-\Delta H^\circ$ (ev)		$h\nu_{CT}$ (ev)		b^2/a^2	
	Tetracycline	Oxytetracycline	Tetracycline	Oxytetracycline	Tetracycline	Oxytetracycline
Adenine	0.42	0.32	3.18	3.13	0.1309	0.1024
Guanine	0.40	0.30	3.10	3.11	0.1278	0.0982
Hypoxanthine	0.33	0.28	3.08	3.09	0.1065	0.0917
Xanthine	0.24	0.26	3.08	3.05	0.0783	0.0851
Thymine	0.39	0.30	3.20	3.14	0 1242	0.0972
Uracil	0.36	0.29	3.23	3.22	0 1116	0.0904
Phenylalanine	0.34	0.30	3.18	3.16	0.1070	0.0967
Tyrosine	0.35	0.32	3.17	3.14	0.1129	0.1021
Histidine	0.28	0.28	3.14	3.13	0.0902	0.0903
Tryptophan	0.25	0.27	3.10	3.20	0.0799	0.0878

Fig. 8

According to Mulliken[17], the ground state and excited state of the molecular complex may be written as

$$\psi_N(DA) = a\psi_0(DA) + b\psi_1(D^+A^-)$$

and $\psi_E(DA) = a^*\psi_1(D^+A^-) - b^*\psi_0(DA)$

where $\psi_0(DA)$ is the no-bond wave function and ψ_1 the dative bond wavefunction. For weak complexes $a \gg b$, $a^* \gg b^*$; moreover $a^* \sim a$ and $b^* \sim b$. The ratio b^2/a^2 can be calculated from the observed heat of formation and position of CT bands following Ketelaar[18] and Tamres and Brandon[8].

$$b^2/a^2 \approx -\frac{\Delta H_0}{h\nu}$$

These values are listed in Tables 4 and 5. It appears that the charge-transfer interactions are of the order of 6-14%.

Acknowledgement

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Formation Constants of the Chelates of 2-Hydroxy-1-Naphthalidene-*ortho*-Fluoroaniline with Some Bivalent Metal Ions

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Potentiometric studies on metal chelates of Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and UO_2^{2+} with 2-hydroxy-1-naphthalidene-*ortho*-fluoroaniline have been carried out. The formation constant, pK_1, of the reagent and the formation constants of its metal chelates have been determined by Bjerrum's method at 25±0.1° and at ionic strength 0.1 *M* in 75 : 25 percent (v/v) dioxane-water medium. *The order of stability of metal chelates* is found to be $UO_2^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$.

A survey of literature indicates that no systematic study of the stabilities of 2-hydroxy-1-naphthalidene-*o*-fluoroaniline and its metal chelates with bivalent metal ions has been carried out. The present communication, therefore, deals with the determination of the stability constants of the chelates of 2-hydroxy-1-naphthalidene-*o*-fluoroaniline in 75% (v/v) dioxane-water medium employing the Calvin-Bjerrum *p*H titration technique as adopted by Irving and Rossotti[1].

Experimental

A precision research *p*H meter, Corning Model 12, with a wide range glass electrode and calomel reference electrode was used for *p*H measurements. The meter has an arrangement for normal and expanded scales. The smallest division on the expanded scale is 0.005 *p*H unit.

The ligand, 2-hydroxy-1-naphthalidene-*o*-fluoroaniline, was prepared and repeatedly crystallised from alcohol to get an analytically pure sample (m.p. 104°). The purity of the ligand was ascertained by elemental analysis. The carbon and hydrogen content of the fluoro compound was determined by the method described by Steyermark[2]. Fluorine was determined by the volumetric procedure of Schoniger[3]. (Found : C, 76.8 ; H, 4.30 ; N, 5.20 ; F, 6.90. Calcd. for $C_{17}H_{12}FNO$; C, 76.98 ; H, 4.53 ; N, 5.28 ; F, 7.17%).

All the chemicals used except the ligand and the perchloric acid were of B. D. H. analytical grade. The perchloric acid was E. Merck G. R. grade. The medium of titration was a 75% (v/v) dioxane-water mixture. The dioxane used was purified by the method described by Vogel[4]. Distilled water, redistilled over alkaline potassium permanganate, was used throughout the investigation. Sodium perchlorate was added to maintain a constant ionic strength (0.1 *M*). The titrations were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the solutions. Metal perchlorates were prepared from the oxides or carbonates and standardised complexometrically by EDTA[5]. Measurements were carried out at 25 ± 0.1°.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide solution (1.01 *M*) :

(i) 5 ml 0.16 *M* $HClO_4$ + 5 ml 0.64 *M* $NaClO_4$ + 30 ml dioxane.

(ii) 5 ml 0.16 *M* $HClO_4$ + 5 ml 0.64 *M* $NaClO_4$ + requisite amount of the reagent to give 0.004 *M* reagent concentration in the final solution + 30 ml dioxane.

(iii) 5 ml 0.64 *M* $NaClO_4$ + 5 ml 0.008 *M* metal salt solution in 0.16 *M* $HClO_4$ + requisite amount of the reagent to give 0.004 *M* reagent concentration in the final solution + 30 ml dioxane.

All titrations were performed in duplicate to test for reproducibility. The results are depicted in Fig. 1.

The experimental method of Irving and Rossotti[1] was applied to find out the values of $\bar{n}$ and *p*L.

Results and Discussion

In the ligand, it is the phenolic OH group that takes part in complex formation and the proton is replaced by metal ions during chelation. Since only one proton per ligand molecule is liberated during complexation, Y, the number of dissociable protons attached per ligand molecule is one.

From the titration curves using solutions (i) and (ii), $\bar{n}_A$ values at various B values (*p*H meter readings) were calculated, and the curve of B against the corresponding $\bar{n}_A$ values was plotted. The formation curve extends over a range $0.18 < \bar{n}_A < 0.97$. This indicates the formation of the species

Fig. 1. Titration curves of 2-hydroxy-1-naphthalidene-*o*-fluoroaniline.
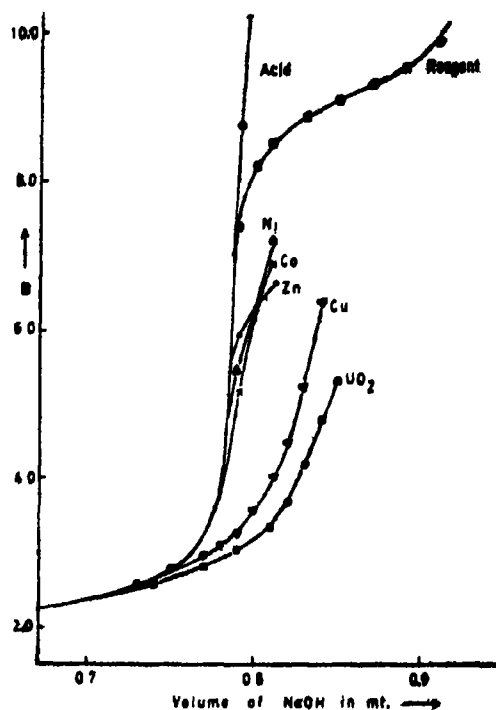
Fig. 2. Formation curves of metal ligand systems of 2-hydroxy-1-naphthalidene-*o*-fluoroaniline.

HL only. The value of pK_1^H could be determined from the half-integral point at $\bar{n}_A = 0.5$.

The maximum values of $\bar{n}$ for Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} systems range from 0.606 to 0.998 indicating the formation of 1 : 1 complexes only. Precipitation in these systems occurs at B=6.4, 7.2, 6.9 and 6.6, respectively. Since the maximum value of $\bar{n}$ obtained at the point of incipient precipitation is 1.0, log K_2 for the above systems could not be determined by the reported method. For UO_2^{2+}, precipitation does not occur till B=5.32 at which point $\bar{n}$ values lie well above 1.5. Both log K_1 and log K_2 could, therefore, be obtained. Since the difference between log K_1 and log K_2 for UO_2^{2+} obtained by the half $\bar{n}$ method was less than 1.78 log units, the least square method was used to obtain refined values.

Fig. 2 shows the experimental data ($\bar{n}$, *pL*) for the metal ligand systems in 75% dioxane-water medium together with theoretical formation curves[5] calculated from the relationship $\bar{n}+(\bar{n}-1)\,K_1(L)+(\bar{n}-2)\,K_1K_2\,(L)^2=0$.

Values of stability constants for all the systems, except UO_2^{2+}, obtained from the half-integral method were used for the above calculation. For UO_2^{2+}, the values of stability constants obtained from the least square treatment were employed. The curve for Cu^{2+} is in appreciably better agreement with the experimental points. A lower precision is indicated for the systems involving Co^{2+} and Ni^{2+}. A more satisfactory agreement for these systems could not be obtained since the values of log K, calculated by the method of successive approximations remained within the limits of error.

The most representative values are recorded in Table 1. Standard deviations[6] and limits of error

TABLE 1—STEPWISE STABILITY CONSTANTS OF THE COMPLEXES OF 2-HYDROXY-1-NAPHTHALIDENE-*o*-FLUOROANILINE WITH SOME BIVALENT METAL IONS

$t = 25 \pm 0.1°$ $\mu = 0.1\ M\ (NaClO_4)$

Cations	H^+	Cu^{2+}	UO_2^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}
log K_1	9.34	8.47	8.96	5.08	5.25	5.40
log K_2	—	—	7.18	—	—	—

For H^+, K_1 corresponds to the species LH, while for metal ions K_1 and K_2 correspond to the species ML_1 and ML_2 respectively.

for log K values range from ± 0.2 to ± 0.03 and ± 0.13 to ± 0.02, respectively. The order of stability for the metal chelates was found to be $UO_2^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$.

Acknowledgement

The authors sincerely thank Dr. D. G. Vartak, B. A. R. C., Bombay for valuable suggestions and Prof. A. P. Rao, Head, Chemistry Dept., Ramnarain Ruia College for encouragement.

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Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-2′,6′-Dimethylaniline Complexes with La^{3+}, Y^{3+}, Pr^{3+}, Nd^{3+}, Dy^{3+} and Gd^{3+}

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Potentiometric studies on metal complexes of La^{3+}, Y^{3+}, Pr^{3+}, Nd^{3+}, Dy^{3+} and Gd^{3+} with 2-hydroxy-1-naphthalidene-2′,6′-dimethylaniline have been carried out. The proton-ligand dissociation constants (pK_1 and pK_2) of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at 25±0.1° and at an ionic strength 0.1*M* ($NaClO_4$) in 75 : 25 percent (v/v) dioxane-water medium. The validity of Born's relation was examined by studying the plot of Z^2/r vs log K values of rare earth complexes of the ligand.

THE successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-2′,6′-dimethylaniline with trivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum *p*H titration technique as adopted by Irving and Rossotti[1] and the findings are reported in the present communication.

A precision research *p*H meter, Corning Model 12, with combined glass electrode and a calomel reference electrode was used for *p*H measurements. Both the electrodes dip into the titration mixture without vitiating any results. The meter has an arrangement for normal and expanded scales and the *p*H can be measured with an accuracy of 0.005 *p*H unit.

Experimental

The ligand, 2-hydroxy-1-naphthalidene-2′,6′-dimethylaniline was prepared and repeatedly crystallised from alcohol to get an analytically pure sample with m.p. 116° (observed).

The dioxane used was purified by the method described by Vogel[2]. Distilled water, redistilled over alkaline potassium permanganate, was used throughout the investigation.

The medium of titration was 75 : 25 per cent dioxane-water (v/v) mixture. Sodium perchlorate was added to maintain a constant ionic strength. The titrations were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the solutions. The free acid, the free acid plus the ligand and the mixture of metal ion, the acid and the ligand were titrated against standard carbonate free sodium hydroxide. Metal ion solutions of yttrium, gadolinium and neodymium were prepared by taking metal nitrates of A.R. grade which were converted to their respective carbonates and then to their perchlorates. Metal ion solutions of dysprosium, praseodymium and lanthanum were prepared by taking the metal carbonates of A. R. grade which were converted to their respective perchlorates. The metal nitrates and carbonates were supplied by S. D. Lab. Chem. Industry, Bombay. All the solutions were standardised complexometrically[3] by EDTA titrations. All measurements were carried out at 25 ± 0.1°.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.07 *M*) solution :

(i) 5 ml 0.16 *M* $HClO_4$+5 ml 0.64 *M* $NaClO_4$+ 30 ml dioxane.

(ii) 5 ml 0.16 *M* $HClO_4$ + 5 ml 0.64 *M* $NaClO_4$ + 60.0 mg reagent to give 0.004 *M* reagent concentration in the final solution +30 ml dioxane.

(iii) 5 ml 0.64 *M* $NaClO_4$ + 5 ml metal salt 0.008 *M* solution in 0.16 *M* $HClO_4$ + 60.0 mg reagent to give 0.004 *M* reagent concentration in the final solution + 30 ml dioxane.

The appropriate correction factor for converting *p*H meter readings (B values) to $-\log[H^+]$ in 75% (v/v) dioxane-water was applied[4] and the curves plotted accordingly. The experimental method of Irving and Rossotti[1] was applied to find out values of $\bar{n}$ and *p*L. The titrations were performed in duplicate to test for reproducibility.

Results and Discussion

It may be pointed out here that the ligand used in this study did not undergo hydrolysis under the experimental conditions. This was indicated by rapid attainment of equilibrium during titration and by the absence of any significant drift in the *p*H even after 1 hr. In the ligand, it is the phenolic OH group that takes part in complex formation and the ligand behaves as a monoprotoic one.

From the titration curves using the solutions (*i*) and (ii), $\bar{n}_A$ values at various *p*H were calculated and a curve between *p*H and the corresponding $\bar{n}_A$ values was plotted (Fig. 1). The values of pK_1^H and pK_2^H were evaluated by the half-integral method as well as from the plots of log $\bar{n}_A/1-\bar{n}_A$ vs *p*H and log $(2-\bar{n}_A)/(\bar{n}_A-1)$ vs *p*H (Figs. 2 and 3). Both these values agree well.

From the titration curves of solutions (ii) and (iii), $\bar{n}$ and *p*L values were calculated. The $\bar{n}$ values were plotted against the corresponding *p*L values to get the formation curves of metal complex ion equilibria (Fig. 4). For lanthanum and praseodymium metal systems, log K_1 and log K_2 values were evaluated by the half-integral method. These values agree well with those obtained from
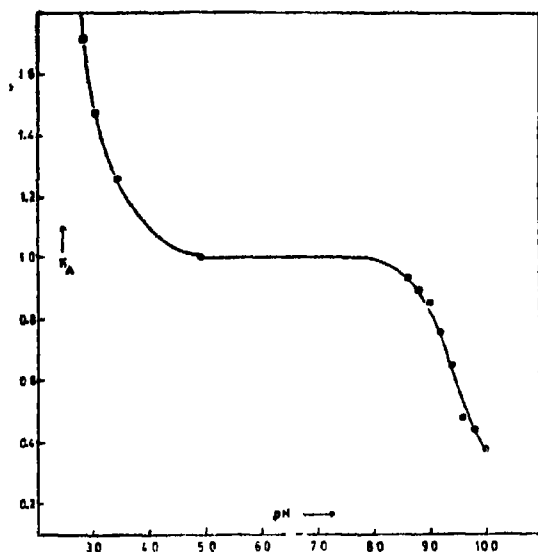
Fig 1. Formation curve of 2-hydroxy-1-naphthalidene-2',6'-dimethylaniline. Plot of $\bar{n}_A$ vs *p*H
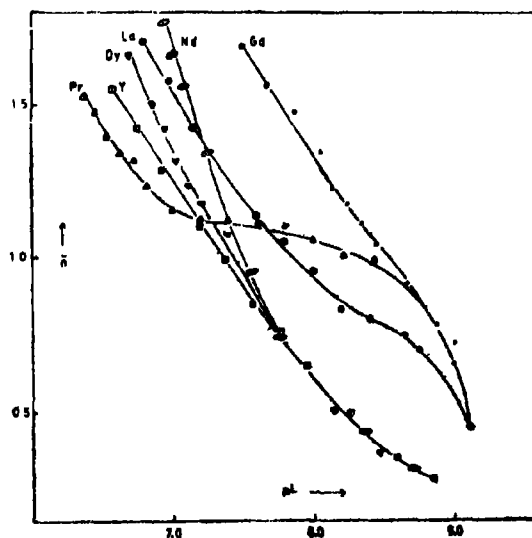
Fig 4. Metal ligand systems of 2-hydroxy-1-naphthalidene-2',6'-dimethylaniline. Plot of $\bar{n}$ vs *p*L
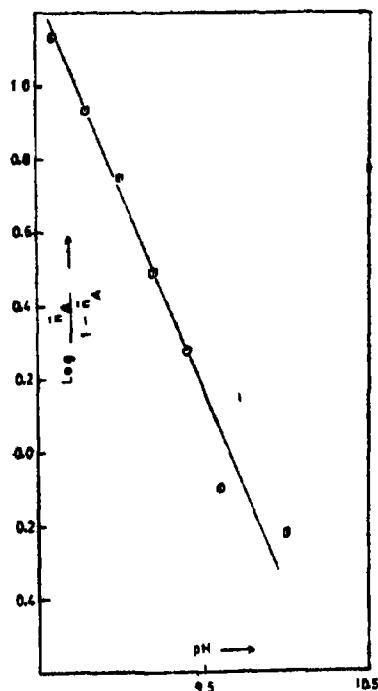
Fig. 2. 2-Hydroxy-1-naphthalidene-2',6'-dimethylaniline. Plot of log $\bar{n}_A/1-\bar{n}_A$ vs *p*H
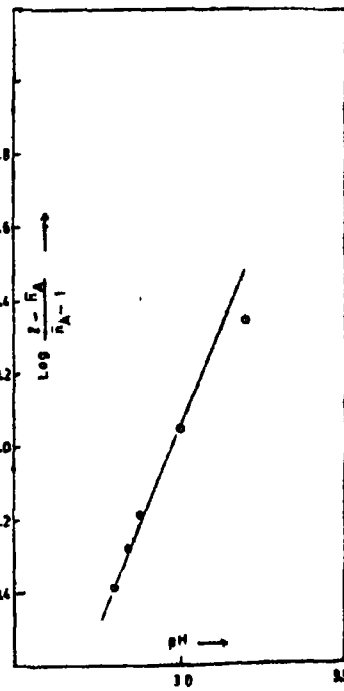
Fig. 3. 2-Hydroxy-1-naphthalidene 2',6'-dimethylaniline. Plot of log $2-\bar{n}_A/\bar{n}_A-1$ vs *p*H.
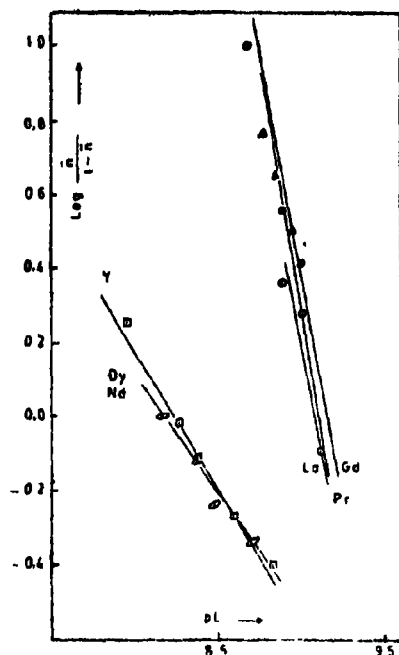
Fig. 5 2-Hydroxy-1-naphthalidene-2',6'-dimethylaniline Plot of log $\bar{n}/1-\bar{n}$ vs pL
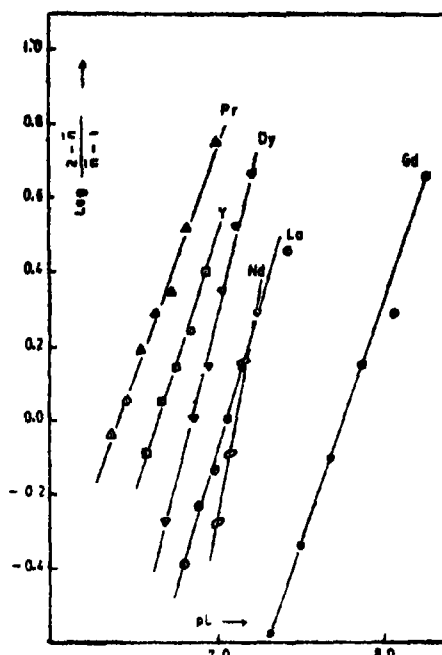
Fig. 6 2-Hydroxy-1-naphthalidene-2',6'-dimethylaniline. Plot of log $2-\bar{n}/\bar{n}-1$ vs pL

TABLE 1—STEPWISE STABILITY CONSTANTS OF THE COMPLEXES OF 2-HYDROXY-2',6'-DIMETHYLANILINE WITH TRIVALENT LANTHANIDES

$t = 25 \pm 0.1°$ $\mu = 0.1$ $(NaClO_4)$

Cations	H^+	Y^{3+}	La^{3+}	Pr^{3+}	Nd^{3+}	Dy^{3+}	Gd^{3+}
log K_1	9.65	8.19	9.06	9.10	8.09	7.87	9.21
log K_2	2.97	6.90	7.06	6.42	7.13	7.15	7.80
σ^5	±0.025	±0.058	±0.058	±0.058	+0.07	+0.13	±0.038
Limits of error	±0.018	±0.04	±0.03	+0.03	±0.01	±0.07	±0.03

For proton association (H^+) K_1 corresponds to the species LH, while for metal ions, K_1 and K_2 correspond to the species ML_1 and ML_2, respectively

the linear plots of log $\bar{n}/1-\bar{n}$ and log $2-\bar{n}/\bar{n}-1$ vs pL (Figs. 5 and 6). In the case of metal systems of neodymium, yttrium, dysprosium and gadolinium, where the difference between log K_1 and log K_2 values was found to be less than 1.78 log unit, the same were calculated by the least square method. The most representative values are recorded in Table 1. Standard deviations range from 0.04 to 0.13, the lower precision being observed for dysprosium. Limits of error lie between ± 0.03 and ± 0.07. The order of stability of the trivalent metal chelates was found to be Gd > La > Pr > Y > Nd > Dy.

Rare earths normally form ionic compounds. The possibility of covalent interaction, however, cannot be completely excluded as reported in the case of acetylacetone chelates of rare earths[6]. If the bonds are ionic, the Born relation $E = Z^2/2r(1-1/D)$ should hold for the energy change on complexation of a gaseous ion of charge Z and radius r in a medium of dielectric constant D. Since the stability constant is related directly to this energy, the log K values should increase linearly with Z^2/r. The plots of log K_1 vs Z^2/r values of the rare earth complexes do not exhibit any linear increase of log K_1 with increase in Z^2/r.

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The authors sincerely thank Dr. D. G. Vartak, B. A. R. C., Bombay, for valuable suggestions and Prof. A. P. Rao, Head of Chemistry Department, Ramnarain Ruia College, for continuous encouragement.

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Determination of Stability Constants of 2-Hydroxy-1-Naphthalidene-4'-Hydroxyaniline Complexes with Mg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}

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Manuscript received 6 August 1981, accepted 1 May 1982

Potentiometric studies on metal complexes of Mg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} with 2-hydroxy-1-naphthalidene-4'-hydroxyaniline have been carried out. The proton-ligand dissociation constants (pK_1 and pK_2) of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at 25 ± 0.1° and at an ionic strength 0.1 *M* in 75 : 25 percent (v/v) dioxane-water medium.

THE successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-4'-hydroxyaniline with bivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum *p*H titration technique as adopted by Irving and Rossotti[1] and the results are presented here.

A precision research *p*H meter, Corning Model 12, with combined glass electrode and a calomel reference electrode was used for *p*H measurements. Both electrodes dip into the titrating mixture without vitiating any results. The meter has an arrangement for normal and expanded scales. The changes in the *p*H can be measured with an accuracy of 0.005 *p*H unit.

Experimental

The ligand 2-hydroxy-1-naphthalidene-4'-hydroxyaniline was prepared and repeatedly crystallised to obtain an analytically pure sample with m.p. 224° (Lit. m.p. 224°)[2].

The dioxane used was purified by the method described by Vogel[3]. Distilled water redistilled over alkaline potassium permanganate was used throughout the investigation.

The medium of titration was 75 : 25 per cent dioxane-water (v/v) mixture. A constant ionic strength was maintained by adding sodium perchlorate. The titrations were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through the solutions. The free acid, the free acid plus the ligand and the mixture of metal ion containing the acid plus the ligand were titrated against standard carbonate free sodium hydroxide. Metal ion solutions of nickel and magnesium were prepared by taking the metal carbonates of A. R. grade, and those of copper and zinc were prepared by taking the metal oxides of A. R. grade. These were standardised complexometrically[4] by EDTA titrations. All measurements were carried out at 25 ± 0.1°.

The following solutions were titrated potentiometrically against standard carbonate free sodium hydroxide (1.07 *M*) solution.

(i) 5 ml 0.16 *M* $HClO_4$ + 5 ml 0.64 *M* $NaClO_4$ + 30 ml dioxane.

(ii) 5 ml 0.16 *M* $HClO_4$ + 5 ml 0.64 *M* $NaClO_4$ + requisite amount of reagent to give 0.004 *M* reagent concentration in the final solution + 30 ml dioxane.

(iii) 5 ml 0.64 *M* $NaClO_4$ + 5 ml metal salt 0.008 *M* solution in 0.16 *M* $HClO_4$ + the requisite amount of the reagent to give 0.004 *M* reagent concentration in the final solution + 30 ml dioxane.

The experimental method of Irving and Rossotti was applied to find out the value of $\bar{n}$ and *p*L. The titrations were performed in duplicate to test for reproducibility.

Results and Discussion

It may be pointed out here that the ligand used in this study did not undergo hydrolysis under the experimental conditions. This was indicated by rapid attainment of equilibrium during the titration and by the absence of any significant drift in the *p*H even after 1 hr.

In the ligand, it is the phenolic OH group that takes part in the complex formation and the ligand behaves as monoprotoic.

From the titration curves using the solutions (i) and (ii), $\bar{n}_A$ values at various B values, (*p*H meter readings), were calculated and a curve between B and the corresponding $\bar{n}_A$ values was plotted (Fig. 1). The value of pK_1^H was evaluated by half integral method as well as from the plot of $\log \left[\frac{\bar{n}_A}{1-\bar{n}_A}\right]$ vs B (Fig. 2). Both these values agree well.

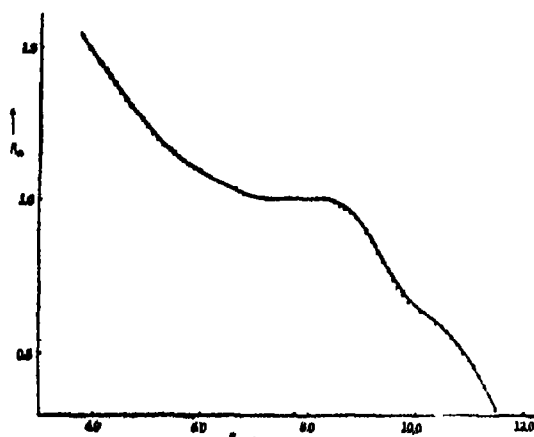



Fig. 1. Formation curve of 2-hydroxy-1-naphthalidene-4'-hydroxyaniline. Plot of $\bar{n}_A$ vs B

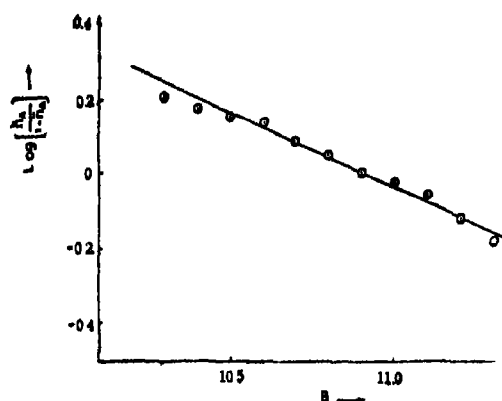



Fig 4 Metal ligand systems of 2-hydroxy-1-naphthalidine-4'-hydroxyaniline. Plot of $\bar{n}$ vs pL

Fig. 2 2-Hydroxy-1-naphthalidene-4'-hydroxyaniline Plot of $\log\left[\frac{\bar{n}_A}{1-\bar{n}_A}\right]$ vs B

Fig 5 2-Hydroxy-1-naphthalidene-4'-hydroxyaniline Plot of $\log\left[\frac{\bar{n}}{1-\bar{n}}\right]$ vs pL

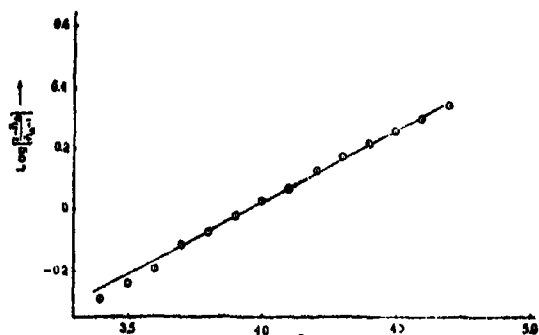



Fig. 3. 2-Hydroxy-1-naphthalidene-4'-hydroxyaniline. Plot of $\log\left[\frac{2-\bar{n}_A}{\bar{n}_A-1}\right]$ vs B

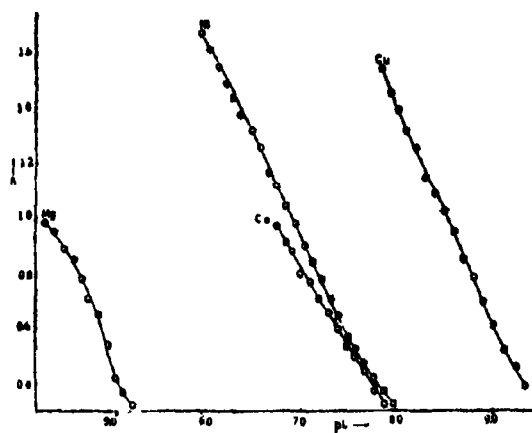
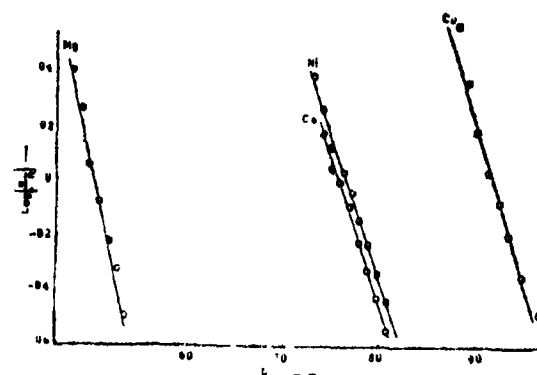
From the titration curves of solutions (ii) and (iii) $\bar{n}$ and pL values were calculated. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of metal complex ion equilibria. From this $\log K_1$ and $\log K_2$ values were evaluated by the half integral method. In the case of nickel and copper systems, the difference between $\log K_1$ and $\log K_2$ values was found to be less than 1.78 log unit and hence these were calculated by the least square method and are reported.

The most representative values are recorded in Table 1. The order of stability of the various metal chelates was found to be $Cu^{2+} > Co^{2+} \approx Ni^{2+} > Mg^{2+}$. This is in agreement with Murakami order[6].

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES

t = 25° μ = 0.1

Cations	H^+	Mg^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$\log K_1$	10.98	5.00	7.57	7.57	9.08
$\log K_2$	3.94	—	—	6.29	7.99

For proton association (H^+), K_1 corresponds to the species LH, while for metal ions K_1 and K_2 correspond to the species ML_1 and ML_2, respectively.

Acknowledgement

The authors record sincere thanks to Dr. D. G. Vartak, B. A. R. C., Bombay for valuable suggestions

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Studies on the Polarographic Reduction of Progesterone

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Progesterone gave a well defined slightly drawnout wave when studied polarographically. The process is irreversible and a continuous negative shift in $E_{1/2}$ is observed with increasing pH. The value of $k_{f,h}D^{-1/2}$ varies from 0.016 to 5 348 at the foot of the wave to the plateau indicating that the process is completely kinetically controlled at the foot of the wave but becomes diffusion controlled and reversible at the plateau. A tentative mechanism for the reduction process has been proposed.

THE direct polarographic reduction of conjugated keto steroids has been studied earlier[1] and it is reported that ketones with a conjugated double bond are directly reducible at the d. m. e. Wolfe, Hershberg and Fieser (*loc. cit.*) were the pioneers in the polarography of keto steroids and they introduced a method for assaying the 17-keto steroid. Eisenbrand and Picher[2] found it possible to determine polarographically some hormones such as, testosterone, progesterone, corticosterone and desoxycorticosterone, which contain keto group and conjugated double bonding O=C–C=C–. Barnett and Morris[3] studied some water soluble steroidal hydrazones polarographically.

The polarographic reduction of keto steroids depends greatly on external factors such as *p*H, nature and concentration of buffer and solvent. Much of the early work on the α,β-unsaturated keto steroid was performed in unbuffered or poorly buffered systems. Adkins and Cox[4] obtained reduction waves for cholesterone in 0.1 *N* ammonium chloride solutions. Later, Eiesenbrand and Picher (*loc. cit.*) observed the behaviour of several Δ^4-3-keto steroid in 90% ethanol and 0 1 *N* LiCl.

Sartori and Bianchi[5] reported the half wave dependence on *p*H for 17-ethinyl-testosterone and methyl testosterone, but did not describe any changes in the wave form or diffusion current with *p*H. Later, Zuman *et al*[6] made a fairly exhaustive study on the behaviour of certain Δ^4-3-keto steroids in 30-60% ethanol solutions buffered with Britton and Robinson buffer mixtures.

The present paper deals with the polarographic behaviour of a conjugated keto steroid, progesterone, in presence of phosphate buffer. The study has been carried out in two different supporting electrolytes, LiCl and KCl, and an attempt has been made to suggest a mechanism for the reduction process.

Experimental

Pure sample of progesterone (B. D. H.) was used in all the experiments. All other chemicals were of B. D. H. AR grade. Solutions were prepared in double distilled water and were deaerated by bubbling pure nitrogen gas. The temperature was maintained at 15 ± 0.1° using a thermostat.

Polarograms were taken at different *p*H by using phosphate buffer in presence of KCl or LiCl used as supporting electrolyte. A Toshniwal manual polarograph, in conjunction with a sensitive polyflex galvanometer was used. The half wave potential refers to the saturated calomel electrode (S.C.E). Pure distilled mercury was used in dropping mercury electrode and the capillary characteristics at mercury height of 35 cm was $m^{2/3}\,t^{1/6} = 2.031$ $mg^{2/3}\,sec^{-1/2}$ in 0.1 *N* KCl.

Results and Discussion

A well defined single step reduction of progesterone is observed when it is reduced at the d. m. e. The diffusion current varies linearly with increase in the concentration of progesterone and the plots of i_d vs $\sqrt{h_{corr}}$ indicate the phenomenon as diffusion controlled.

Analysis of C - V curves indicates the irreversibility of the process which is further confirmed by the nature of log plots and the value of $E_{3/4} - E_{1/4}$ (Table 1 ; Fig. 1) ; when log $(i - i_r)$ is plotted against $-E_{d.e.}$ an initial straight line followed by a curve, a characteristic of irreversible process, is obtained. The values of the product of transfer coefficient and the number of electrons involved in the reduction process, αn, have been determined (Table 1) which are in conformity with the irreversible nature of the reduction process.

The diffusion current is markedly affected by the nature of the supporting electrolyte and the half wave potential is almost the same in both the supporting electrolytes (–0.92 V vs S.C.E.). The half wave potential is unaffected by the concentration of the depolarizer. However, it changes with temperature, first it increases and then decreases with the rise in temperature. All the while, the temperature coefficient of half wave potential is more than 2 mV per degree as can be expected of an irreversible process. The diffusion current varies linearly with temperature and the temperature coefficient is 0.0903 μ amp per degree.

TABLE 1

Conc. of progesterone = 2.4×10^{-3} %
Hg height = 85 cm
Temp. = $15 \pm 0.1°$
Buffer = Phosphate buffer (Na_2HPO_4 and NaH_2PO_4)

Supporting electrolyte	0.1 *M* LiCl				0.1 *M* KCl			
pH	i_d (μA)	$-E_{1/2}$ (Volts)	$E_{3/4}-E_{1/4}$ (Volts)	αn	i_d (μA)	$-E_{1/2}$ (Volts)	$E_{3/4}-E_{1/4}$ (Volts)	αn
5.8	0.9030	0.84	0.14	0.1564	1.0960	0.88	0 16	0.2513
6.2	0.8382	0.84	0 20	0.1281	0 9997	0.89	0.18	0.1774
6.4	0.8062	0.88	0.22	0.1625	0 9675	0 90	0.20	0.1922
6.8	0.7417	0 90	0 26	0 1186	0 9030	0.90	0.24	0.2809
7.4	0.7095	0.92	0.22	0.1182	0.7417	0.92	0 24	0 1478
7.8	0.6450	0.96	0 28	0.1106	0.6450	0.94	0.26	0.1774
8.1	0.6127	0.98	0.28	0.1184	0.5808	0.98	0.28	0.1922

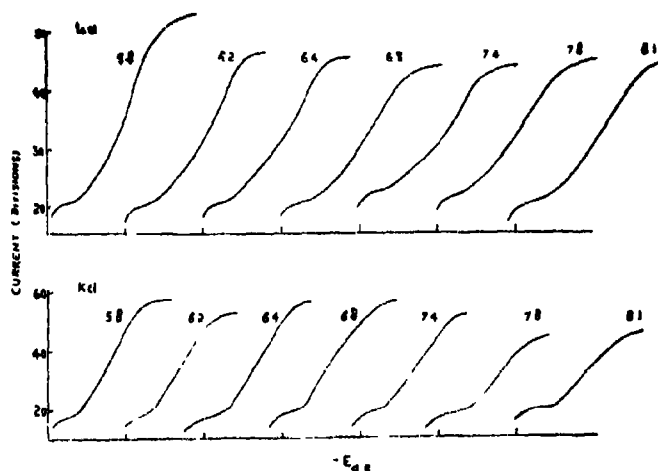



Fig 1. C = V curves of progesterone at different pH

A regular negative shift in half wave potential and decrease in diffusion current with increasing pH has been observed and a strict proportionality of both the factors with pH has been obtained (Figs. 2, 3) The negative shift of half wave potential and the decrease in the value of the diffusion current may be due to the complexation of the depolarizer with the constituents of buffer.

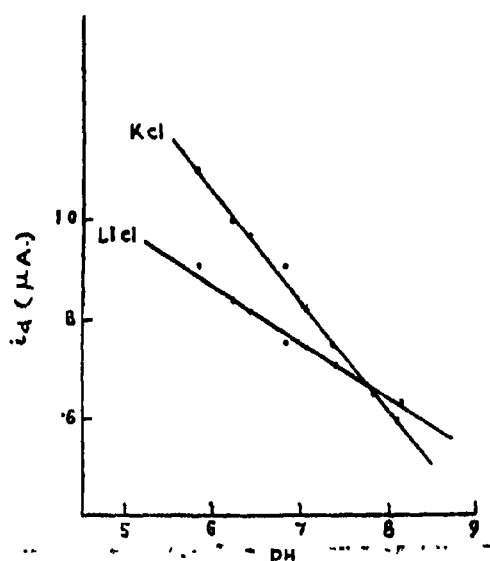



Fig. 2. pH vs i_d.

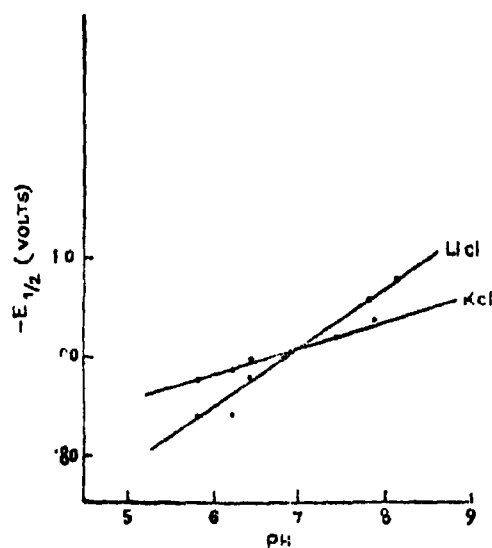



Fig. 3. pH vs $-E_{1/2}$.

The values of the rate constant $k_{f,h}$ at different potentials have been calculated by Koutecky's method[7]. An increase in the value of $k_{f,h}$ with potential is observed and $-\log k_{f,h}$ vs $-E_{d.e.}$ plots are straight lines (Fig. 4). The value of $k_{f,h}\,D^{-1/2}$ varies from 0.016 to 5.348 (Table 2) with the increase in potential at the d. m. e. which clearly indicates that the electrode process is totally irreversible and kinetically controlled at the foot of the wave while it is reversible and diffusion controlled at the top. During the entire rising portion of the wave the process is controlled kinetically and by diffusion. The value of heterogeneous rate constant $k^{0}_{f,h}$ increases regularly with the increase in *p*H, indicating that the phenomenon becomes more and more reversible. The variation in free energy change with *p*H also supports this view. The value of $k^{0}_{f,h}$ first increases and then decreases with a rise in temperature and the value at 25° is maximum. This variation is in accordance with the shift in $E_{1/2}$ with temperature (Table 3).

Mechanism of polarographic reduction : Progesterone molecule possesses conjugated carbonyl group at 3-C atom and therefore, the electrolytic

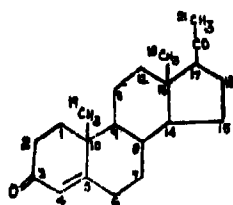
Fig. 4. $-\log k_{f,h}$ vs $-E_{d.e.}$

TABLE 2

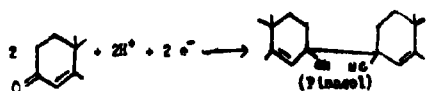
Supp. electrolyte *p*H	0.1 *M* LiCl $-E_{d.e.}$ (V)	$-\log k_{f,h}$	$k_{f,h}\times10^{5}$	$k_{f,h}\times D^{-1/2}$	$k^{0}_{f,h}\times10^{9}$ (cm sec^{-1})	ΔG (K cal)	0.1 *M* KCl $-E_{d.e.}$ (V)	$-\log k_{f,h}$	$k_{f,h}\times10^{5}$	$k_{f,h}\times D^{-1/2}$	$k^{0}_{f,h}\times10^{9}$ (cm sec^{-1})	ΔG (K cal)
5.8	0.5	4.7212	1.90	0.03042			0.7	4.3208	1.20	0.01921		
	0.6	4.6020	2.50	0.04003			0.8	3.9871	10.30	0.01649		
	0.7	4.2291	5.90	0.09447	3.1623	72.7955	0.9	3.6602	21.80	0.05860	3.1623	72.7955
	0.8	3.8181	15.20	0.24339			1.0	3.3056	49.40	0.79103		
	0.9	3.4685	34.20	0.54763			1.1	3.0079	98.00	1.56925		
6.2	0.5	4.7055	1.97	0.03154			0.7	4.4962	3.10	0.05108		
	0.6	4.4089	3.90	0.06244			0.8	4.0640	8.60	0.06507		
	0.7	4.1988	6.40	0.10248	4.4668	71.9287	0.9	3.6223	23.80	0.38206	5.0119	71.6397
	0.8	3.9208	12.90	0.20680			1.0	3.3453	45.10	0.72281		
	0.9	3.4229	47.20	0.75580			1.1	2.9375	115.4	1.84147		
6.4	0.5	4.7212	1.99	0.03186			0.7	4.1898	3.23	0.05172		
	0.6	4.2676	5.40	0.08646			0.8	3.9847	10.35	0.16573		
	0.7	4.0861	8.20	0.06542	6.3096	71.0619	0.9	3.6500	22.38	0.35836	7.9433	70.4840
	0.8	3.8860	13.70	0.21937			1.0	3.1486	71.83	1.15020		
	0.9	3.5528	28.80	0.44835			1.1	2.7945	254.3	4.06725		
6.8	0.5	4.6989	2.00	0.03202			0.7	4.6020	2.50	0.04003		
	0.6	4.4948	3.20	0.05124			0.8	3.9628	10.09	0.16156		
	0.7	4.2144	6.10	0.09767	7.9433	70.4840	0.9	3.7841	16.43	0.25620	25.0000	67.5946
	0.8	3.8258	11.20	0.35068			1.0	3.5048	31.27	0.50072		
	0.9	3.6595	21.90	0.57966			1.1	3.3120	48.74	0.78046		
7.4	0.5	4.6615	2.18	0.03490			0.7	4.5406	2.88	0.04611		
	0.6	4.4698	3.39	0.05428			0.8	4.2168	3.04	0.04867		
	0.7	4.2021	6.2[illegible]	0.10040	14.000	69.039	0.9	3.9309	11.72	0.18767	50.000	65.8609
	0.8	3.9290	11.75	0.18815			1.0	3.6822	32.92	0.52746		
	0.9	3.6988	20.00	0.32025			1.1	3.4899	64.57	1.03394		
7.8	0.5	4.7178	1.90	0.03069			0.7	4.3191	2.40	0.03849		
	0.6	4.6182	2.40	0.03848			0.8	4.1528	7.01	0.11234		
	0.7	4.4105	3.80	0.06222	17.000	68.5192	0.9	3.8711	13.45	0.21537	79.000	64.7052
	0.8	4.1419	7.20	0.11548			1.0	3.5442	28.55	0.36597		
	0.9	3.8576	13.80	0.20816			1.1	3.2478	71.14	1.13713		
8.1	0.5	4.7117	1.90	0.03106			0.7	4.4462	1.55	0.05729		
	0.6	4.5905	2.50	0.04110			0.8	4.2239	11.17	0.09552		
	0.7	4.3822	4.10	0.06642	50.000	65.8609	0.9	3.9586	20.36	0.17886	126.000	63.5494
	0.8	4.1126	7.70	0.12355			1.0	3.7085	49.19	0.78778		
	0.9	3.8188	15.10	0.24823			1.1	3.4000	125.88	2.00160		

TABLE 3

Conc. of progesterone = $1.6 \times 10^{-?}$ %
Hg height = 35 cm
pH = 7.4

Supporting electrolyte	0.1 *M* LiCl				0.1 *M* KCl			
Temp. (°C)	i_d (μ A)	$-E_{\frac{1}{2}}$ (Volt)	$k^0_{f,h} \times 10^?$ (cm. sec^{-1})	ΔG (K cal)	i_d (μ A)	$-E_{\frac{1}{2}}$ (Volt)	$k^0_{f,h} \times 10^?$ (cm. sec^{-1})	ΔG (K cal)
15	0.7740	0.90	5.0119	68.75038	0.8062	0.90	5.0119	71.63978
20	0.9330	0.96	6.3096	71.06190	0.8757	0 92	6 3096	71.06190
25	0.9675	0.98	40.0000	66.43886	0 9352	0.94	16.0000	68.75038
30	1.3867	0.92	32.0620	67.01674	1 2320	0 90	13.0000	69 82826
35	1.4500	0.90	7.9433	70 48402	1 4512	0.86	7 9433	70 48402

Progesterone

reduction of this molecule can take place in a manner similar to that of unsaturated conjugated ketones. One electron bimolecular reduction process is possible which proceeds through a coupling reaction resulting in the formation of a pinacol.

$$2\,[\text{ketone}] + 2H^+ + 2e^- \longrightarrow \text{(Pinacol)}$$

The probability of reduction of second carbonyl group attached at 20-C atom is comparatively less because this carbonyl group lacks conjugation and is sterically more hindered than carbonyl group of C-3 atom. Further, this reduction is difficult as it requires more energy for fission of side chain at C-17 atom from the pentenophenanthrene nucleus. Similar mechanism had been proposed by Kabasakalian and McGlotten[8] for the polarographic reduction of Δ^4-3-keto steroids.

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Polarographic Studies on the Effect of Some Ionic and Non-ionic Surfactants on the Kinetics of Irreversible Electrode Processes of Arylazopyrimidine and Arylazopyrazole

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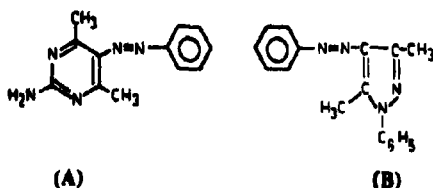
Polarographic behaviour of 2-amino-4,6-dimethyl-5-arylazopyrimidine and N'-phenyl-3,5-dimethyl-4-phenylazopyrazole has been studied in 0.1 *M* KCl in presence of some ionic and non-ionic surfactants. The effect of an increase in surfactant concentration, beyond the concentration just sufficient to eliminate the maxima, on the kinetic parameters of irreversible reduction of arylazopyrimidine and arylazopyrazole has been investigated.

A survey of literature reveals that work on the effect of surfactants on the reaction kinetics of heterocycles at DME is surprisingly scarce[1,2]. Pyrimidines and pyrazoles are of great medicinal and biological importance and a knowledge of the effect of surfactants on their redox behaviour at the solution-mercury interface may prove very useful from the physiological point of view[3]. As surfactants are used as emulsifiers in drugs, the effect of the surfactants on redox behaviour of these compounds is of immense importance. With this aim in view the present study covering totally irreversible electrode processes of 2-amino-4,6-dimethyl-5-arylazopyrimidine (A) and N'-phenyl-3,5-dimethyl-4-arylazopyrazole (B) was undertaken.

(A) (B)

Experimental

Arylazopyrimidine (A) and arylazopyrazole (B) were synthesized by the method reported from this laboratory[4,5]. Stock solutions (1.0×10^{-3} *M*) of compound A and B were prepared in methanol (AnalaR). The buffer used was Britton-Robinson buffers in the *p*H range 2.0-12.0. All the surfactants used were of high purity and their aqueous solutions were employed.

Polarograms were recorded on a Cambridge pen recording polarograph. The capillary characteristic was 2.040 $mg^{2/3}\ sec^{-1/2}$. SCE was used as the reference electrode. For recording polarograms 1.0 ml of stock solution (1.0×10^{-3} *M*) of compound A or B, 1.0 ml of 1.0 *M* KCl, 5.0 ml of buffer and 3.0 ml of water were mixed and a stream of pure nitrogen gas was passed for about 5 min to ensure complete deaeration. The requisite amount of surfactant was added, keeping the volume constant in each case. The cell was kept in a thermostated water both (25 ± 0.1°). The number of electrons involved in the reduction process was calculated by millicoulometry method[6] using $CdSO_4$ as a reference solution. Ilkovic equation was used to calculate the value of diffusion coefficient ($D_0^{1/2}$). The kinetic parameters (αn and $k^{\circ}_{f,h}$) were calculated by Koutecky's treatment[7].

Results and Discussion

Pyrimidine A and pyrazole B gave single, well defined, irreversible diffusion controlled reduction waves whose $E_{1/2}$ were *p*H dependent but i_d remained constant throughout the entire *p*H range. The $E_{1/2}$ was shifted towards negative potential with increase in *p*H thereby showing that protonation precedes reduction.

A perusal of the slope value of log plots reveals that the irreversible reduction of pyrimidine and pyrazole becomes more irreversible when the surfactant is gradually increased beyond the concentration just sufficient to eliminate the maxima. For both the ionic and the non-ionic surfactants, i_d decreases and $E_{1/2}$ records a negative shift (Tables 1 and 2) as their concentration is increased.

The product αn_a shows a decrease with the increase in surfactant concentration. The polarographic reduction of arylazopyrimidine and arylazopyrazole was found to be two electron reduction and therefore αn_a, the number of electron involved in the rate-determining step can either be 1 or 2. Since the decrease in the αn value is indiscrete and at no stage the two consecutive values vary by a factor of 2, the possibility of decrease in value of the product αn_a due to a change in n_a is ruled out. It can thus be safely concluded that it is the α which is decreasing[8,9].

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TABLE 1—EFFECT OF INCREASING CONCENTRATIONS OF IONIC AND NON-IONIC SURFACTANTS ON THE KINETICS OF IRREVERSIBLE ELECTRODE PROCESS OF ARYLAZOPYRIMIDINE AT pH 6.2

Surfactants	(Surfactant) %	$-E_{1/2}$ V	i_d μA	αn_a	$D_o^{1/2} \times 10^6$ cm^2/sec	$k^{\circ}_{f,h}$ cm/sec
Cationic						
CTAB	*1.0×10^{-2}	0.56	1.25	0.62	8.6	1.2×10^{-10}
	1.6×10^{-2}	0.57	1.22	0.60	8.2	8.6×10^{-11}
	2.2×10^{-2}	0.59	1.16	0.57	8.0	5.0×10^{-11}
CPB	*1.4×10^{-2}	0.56	1.25	0.64	8.6	1.2×10^{-10}
	2.0×10^{-2}	0.58	1.20	0.62	8.0	7.2×10^{-11}
	2.6×10^{-2}	0.61	1.14	0.60	7.2	2.2×10^{-12}
Anionic						
SDS	*1.2×10^{-2}	0.56	1.25	0.62	8.6	1.2×10^{-10}
	1.6×10^{-2}	0.59	1.18	0.59	7.8	3.2×10^{-11}
	2.0×10^{-2}	0.62	1.10	0.57	7.0	9.4×10^{-12}
SLS	*1.2×10^{-2}	0.56	1.25	0.64	8.6	1.4×10^{-10}
	1.6×10^{-2}	0.60	1.08	0.61	7.9	1.2×10^{-11}
	2.0×10^{-2}	0.64	1.04	0.58	7.5	8.4×10^{-12}
Non-ionic						
Tween-20	*2.0×10^{-2}	0.56	1.25	0.62	8.67	1.2×10^{-10}
	2.4×10^{-2}	0.58	1.09	0.60	8.2	3.8×10^{-11}
	2.8×10^{-2}	0.62	1.04	0.57	7.7	8.4×10^{-12}
Triton X-100	*2.0×10^{-2}	0.56	1.25	0.64	8.6	1.2×10^{-10}
	2.4×10^{-2}	0.61	1.15	0.62	8.1	3.4×10^{-11}
	2.8×10^{-2}	0.65	1.05	0.60	7.5	8.6×10^{-12}

TABLE 2—EFFECT OF INCREASING CONCENTRATIONS OF IONIC AND NON-IONIC SURFACTANTS ON THE KINETICS OF IRREVERSIBLE ELECTRODE PROCESS OF ARYLAZOPYRAZOLE AT pH 6.2

Surfactants	(Surfactant) %	$-E_{1/2}$ V	i_d μA	αn_a	$D_o^{1/2} \times 10^6$ cm^2/sec	$k^{\circ}_{f,h}$ cm/sec
Cationic						
CTAB	*1.0×10^{-2}	0.62	1.10	0.72	9.2	1.6×10^{-11}
	1.6×10^{-2}	0.63	1.08	0.69	8.8	9.2×10^{-12}
	2.2×10^{-2}	0.64	1.04	0.65	8.2	8.0×10^{-12}
CPB	*1.4×10^{-2}	0.62	1.10	0.72	9.2	1.6×10^{-11}
	2.0×10^{-2}	0.63	1.06	0.69	9.0	8.4×10^{-12}
	2.6×10^{-2}	0.65	1.00	0.65	8.4	3.4×10^{-12}
Anionic						
SDS	*1.2×10^{-2}	0.62	1.08	0.70	9.2	1.6×10^{-11}
	1.6×10^{-2}	0.64	1.04	0.68	8.4	5.6×10^{-12}
	2.0×10^{-2}	0.66	1.00	0.65	7.9	1.0×10^{-12}
SLS	*1.2×10^{-2}	0.62	1.10	0.72	9.2	1.8×10^{-11}
	1.6×10^{-2}	0.65	1.05	0.70	8.8	3.4×10^{-12}
	2.0×10^{-2}	0.68	1.01	0.68	8.4	9.3×10^{-12}
Non-ionic						
Tween-20	*2.0×10^{-2}	0.62	1.10	0.72	9.2	1.6×10^{-11}
	2.4×10^{-2}	0.66	1.05	0.69	8.9	6.2×10^{-12}
	2.8×10^{-2}	0.70	1.00	0.66	8.4	9.8×10^{-13}
Triton X-100	*2.0×10^{-2}	0.62	1.10	0.72	9.2	1.6×10^{-11}
	2.4×10^{-2}	0.66	1.05	0.70	8.7	5.2×10^{-12}
	2.8×10^{-2}	0.70	1.00	0.65	8.2	9.4×10^{-13}

* Concentration of surfactant just sufficient to eliminate the maxima.
CTAB—Cetyltrimethylammonium bromide.
CPB—Cetylpyridinium bromide.
SDS—Sodium dodecyl sulphate.
SLS—Sodium lauryl sulphate.

The transfer coefficient, α, signifies the fraction of the applied voltage which favours the cathodic reduction. A decrease in its value implies that transfer of electrons is made increasingly difficult. In other words, the electrode reaction of arylazopyrazole and arylazopyrimidine is rendered increasingly irreversible as surfactant is increased beyond the concentration just sufficient to eliminate

the maxima. The decrease in the value of $K^{0}_{f,h}$ (Tables 1 and 2) with increasing surfactant concentration lends support to this conclusion.

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4-(2-Pyridylazo) Resorcinol, A Sensitive Amperometric Reagent for Ultramicro Determination of Pr^{3+} and Nd^{3+}

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4-(2-Pyridylazo) resorcinol has been employed successfully as an amperometric reagent for the precise determination of Pr^{3+} and Nd^{3+}. The reagent's sensitivity is high. 0.1409 mg of Pr^{3+} and 0.1442 mg of Nd^{3+} could be detected successfully in 10 ml solution of each ion with an error of less than ±0.8%. The titrations have been performed at pH 6.1 ± 0.02 and an ionic strength of 0.5 M [KCl]. The molar ratio of metal : PAR complexation is found to be 1 : 2. Titrations are not hampered by the presence of fairly large amounts of K^+, Na^+, NH_4^+, Mg^{2+}, Tl^+, Ca^{2+}, Mo^{6+}, Cl^-, ClO_4^-, CH_3COO^-, NO_3^- and SO_4^{2-} ions. Experimental and calculated statistical data support the utility of the method

AMONG the various heterocyclic azo dyes[1] PAN, PAR and TAR have been satisfactorily used for the spectrophotometric[2-4] determination of rare earths. 4-(2-Pyridylazo) resorcinol [abbreviated PAR] has also been used for the determination[5-7] of V^{5+}, Ti^{4+}, In^{3+}, Mn^{2+} and various other ions. The spectrophotometric method is not suitable when precipitation occurs, nor it can be used at the close proximity of the wave length of absorption of complex and the ligand. It may predict wrong stoichiometric ratio of metal · ligand. Keeping this in mind an attempt has been made to estimate Pr^{3+} and Nd^{3+} amperometrically using PAR as a reagent. The present paper deals with the results of amperometric titration of these metal ions with PAR, using d.m.e. as indicator electrode. The method is applicable in presence of various other ions.

Experimental

The chemicals used were of AnalaR or extrapure quality. Pr^{3+} and Nd^{3+} solutions were prepared and standardized[11]. Solution of 4-(2-pyridylazo) resorcinol was prepared by dissolving the requisite quantity of monosodium salt of the reagent (E. Merck) and was standardized potentiometrically[8] in 1 : 1 v/v dioxane-water by standard Pr^{3+} solution. Ionic strength (0.5 *M*) was adjusted with potassium chloride solution. Dil. hydrochloric acid and sodium hydroxide solutions were used to adjust the *p*H at 6.1 ± 0.02.

Amperometric titrations were made on a manually operated polarograph with multiflex galvanometer (sens. 8.10×10^{-9} amp/div), using d.m.e. as indicator electrode and S.C.E. as reference electrode. The capillary used for d.m.e. had a m value of 2.3733 mg/sec at a drop time 3.0 sec in air free 1 *M* potassium chloride solution at 41 cm effective height of mercury column ($m^{2/3} t^{1/6} =$ 2.136 $mg^{2/3} sec^{-1/2}$). An Elico digital *p*H meter (model LI-120) was used for measuring *p*H of the test solutions.

Voltammograms of 4-(2-pyridylazo) resorcinol : The voltammetric studies were carried out on C.I.C., Baroda (India) pen recording polarograph. 4-(2-Pyridylazo) resorcinol gives a well defined polarographic wave at *p*H 6.1 (Fig. 1-A). The polarograms of PAR at different concentrations were recorded and it was found that diffusion current was proportional to the concentration of PAR.
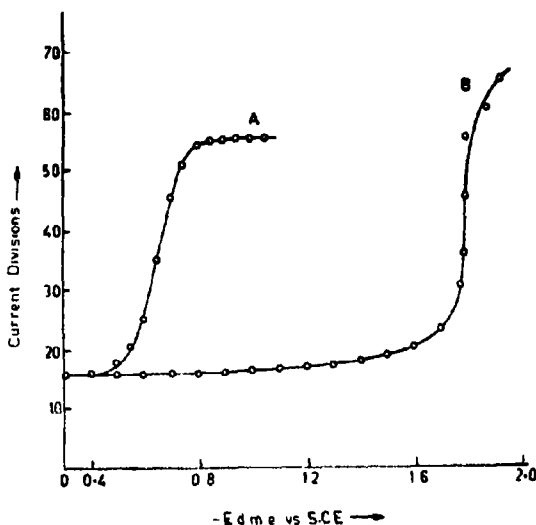
Fig. 1. A : Polarogram of 1 m*M* PAR in 0 5 *M* KCl at *p*H 6 1
B : Polarogram of 2 m*M* metal (Pr^{3+} or Nd^{3+}) in 0.5*M* KCl at *p*H 6 1

Procedure of amperometric titrations : For titrations, sets of solutions containing known amount of Pr^{3+} or Nd^{3+} in 0.5 *M* KCl as supporting electrolyte (in 10 ml volume) were prepared and the *p*H of the solutions were adjusted at 6.1 ± 0.02. The metal solution was taken into the

TABLE 1—AMPEROMETRIC TITRATION OF Pr^{3+} AND Nd^{3+} WITH PAR

Plateau potential = −0.85 V vs S.C.E. ; μ = 0.5 ; pH = 6.1 ± 0.02

Sl No.	Approximate concentration (M)	Amount of Pr^{3+} Taken (mg)	Amount of Pr^{3+} Found* (mg)	% Error	Coefficient of variation*	Amount of Nd^{3+} Taken (mg)	Amount of Nd^{3+} Found* (mg)	% Error	Coefficient of variation*
1.	1×10^{-4}	0.1409	0.1400	−0.63	0.89	0.1442	0.1431	−0.76	0.82
2.	2×10^{-4}	0.2818	0.2834	+0.56	0.85	0.2882	0.2868	−0.48	0.86
3.	4×10^{-4}	0.5636	0.5608	−0.49	0.66	0.5768	0.5798	+0.52	0.70
4.	6×10^{-4}	0.8454	0.8404	−0.59	0.64	0.8652	0.8628	−0.27	0.52
5.	8×10^{-4}	1.1272	1.1298	+0.23	0.81	1.1536	1.1584	+0.41	0.66
6.	1×10^{-3}	1.4091	1.4043	−0.34	0.70	1.4424	1.4494	+0.48	0.86
7.	2×10^{-3}	2.8182	2.8006	−0.62	0.86	2.8848	2.8764	−0.29	0.41
8.	3×10^{-3}	4.2273	4.2456	+0.43	0.41	4.3272	4.3386	+0.26	0.47
9.	4×10^{-3}	5.6364	5.6618	−0.45	0.82	5.7696	5.7320	−0.65	0.70
10.	5×10^{-3}	7.0455	7.0942	−0.69	0.57	7.2120	7.1815	−0.42	0.64

* The values calculated from replicate set of observations for each concentration.

titration cell. The plateau potential [at which Pr^{3+} and Nd^{3+} do not give any diffusion current (Fig. 1-B)] on the wave of PAR i.e., −0.85 V vs S.C.E. was applied and a standard solution of PAR (pH = 6.1 ± 0.02) was added drop by drop from a 1 cm^3 semi micro burette and the current was noted. On plotting galvanometer readings after necessary volume corrections[8] against titrant volumes, reversed L shaped curve was obtained (Fig. 2). The end point indicated a metal to PAR ratio of 1 : 2 which is in good agreement with the spectrophotometric results observed by Munshi and Dey[9]. Similar results were observed by using PAR as titrate and Pr^{3+} or Nd^{3+} as titrant under the identical experimental conditions, but an L shaped curve was obtained in this case.
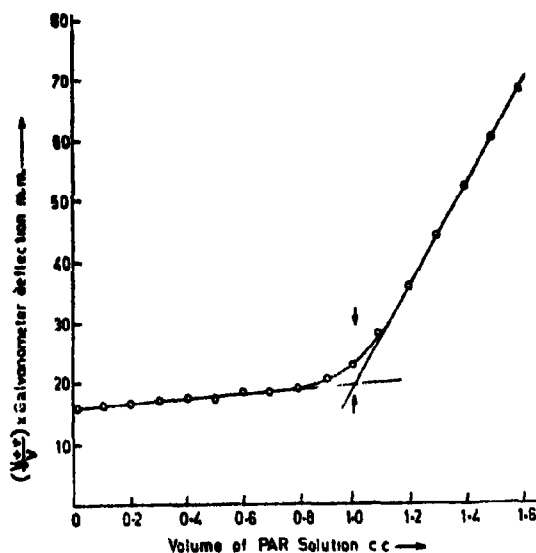
Fig. 2. Amperometric titration curve of Pr^{3+} solution with PAR. Concentration of Pr^{3+} solution taken in cell = 0.001 mM. Concentration of PAR solution = 0.002 mM/ml. V = Volume of Pr^{3+} solution taken in cell i.e. 10 ml. v = Volume of PAR solution added.

Effect of diverse ions: The amperometric titrations of the titled metal ions are not in any way hampered by the presence of fairly large amounts of foreign ions, viz., alkali and alkaline earth metal ions, NH_4^+, Tl^+, Cr^{3+}, Mo^{6+}, Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}, CH_3COO^- etc. However, it is found that small amounts of CO_3^{2-}, PO_4^{3-}, Cd^{2+}, Bi^{3+}, Pb^{2+}, Sb^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} interfere seriously in this titrimetric method.

Results and Discussion

The results of amperometric titrations of the titled metal ions are shown in Table 1. The results indicate that PAR is a sensitive reagent for ultramicro determination of Pr^{3+} and Nd^{3+}. The minimum amount (nearly 0.14 mg) of each of the said metal ions can be estimated successfully with a practical error of less than ±0.8%. In our earlier communications, we reported that Pr^{3+} and Nd^{3+} could be estimated upto 0.70 mg using cupferron[10], ARS[11] and XO[12] as amperometric reagents. The present results clearly show the sensitivity of PAR over these reagents. The low detection limit of PAR is nearly 5 times to that observed with the other three reagents. The repeated experimental observations and finally calculated statistical values like coefficients of variation show the accuracy and precision of the method. It is found that the value of coefficient of variation never exceeded 0.9.

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Structure of Faceted Naphthalene-Benzoic Acid Eutectic

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Microstructure studies of naphthalene-benzoic acid eutectic have shown it to be a faceted-faceted structure in agreement with the recent classification of the eutectics. X-ray studies of the eutectic have shown that certain interplanar distances and the intensities of the reflections in the solidified eutectic differ markedly from those of the pure components, indicating a preferential orientation between the components in the eutectic.

According to the classification given by Jackson and Hunt[1], micromorphologies depend on the entropy of fusion of the pure components; the high entropy constituents form an eutectic having irregular (faceted) growth from the melt. Little has been studied about such faceted eutectics[2] and hence naphthalene-benzoic acid system, in which both the components have a high entropy of fusion, has been chosen for study. Growth kinetics and the structure of the liquid eutectics have also been studied recently[3]. Hogan[4] showed a unique crystallographic orientation relationship between constituent phases and their mating planes. Perfect lamellar grains have been found in lamellar Sn – Cd eutectic by Gruzleski and Winegard[5] but in a number of systems, the eutectic grains do not exhibit a fixed crystal orientation with respect to external lines of forces. Recently, it has been shown that certain frequencies in the ir spectra of naphthalene-benzoic acid eutectic are restricted, showing thereby that there is a specific orientation between the constituents with respect to each other in this composite material[6]. In the present investigation, microscopic, X-ray and D.S.C. studies of naphthalene-benzoic acid eutectic has been made and it has been further established that there is orientation of some of the planes of the new composite formed.

Experimental

Naphthalene (U.S.S.R.) was purified by sublimation and benzoic acid (A.R., B.D.H., London) was taken as such. Purity of naphthalene (m.p. 80.30°) and benzoic acid was checked by the determination of their melting points. Accurately weighed naphthalene and benzoic acid were taken in a tube which was then sealed to avoid evaporation. The material in the tube was melted and then suddenly chilled in ice cold water. This process of melting and chilling was repeated 4-5 times. The tube was then broken and the solid mixture thus formed was powdered using agate mortar and pestle. The phase diagram of naphthalene-benzoic acid system was determined by thaw point method. Eutectic was formed at 0.667 mole fraction of naphthalene with its eutectic point at 69.1°. The accuracy in determining the eutectic point was ±0.1°.

A small amount of the eutectic or that of the pure components was taken on a clean glass slide and carefully melted. A cover slip was then glided over it. These glass slides were then observed under microscope. The heat of fusion of the eutectic and the pure components were determined using differential scanning calorimeter, DSC IB, Perkin Elmer, USA in N_2 atmosphere. These were found to be 32.2, 33.4 and 29.4 cal/g for naphthalene, benzoic acid and the eutectic, respectively.

The X-ray analysis of the eutectic and the pure components was carried out by powder method using Debye Scherrer camera with nickel filtered copper ($K\alpha$) radiation. The intensities of X-ray lines were determined by visual comparison of the lines with the standard intensity scale which had been prepared previously.

Results and Discussion

(a) *Microscopic and D.S.C. studies :* Hunt and Jackson[7] argued that the type of growth of an eutectic depends upon a factor α. Non-faceted growth occurs when $\alpha < 2$, whereas faceted growth occurs when $\alpha > 2$.

$$\alpha = \xi \frac{\Delta S_f}{R}$$

where $\Delta S_f/R$ is the entropy of fusion in dimensionless units and ξ is a crystallographic factor depending upon the geometry of the molecule and is less than or almost equal to one. Benzoic acid and naphthalene have $\Delta S_f/R$ values of 5.25 and 6.45, respectively (ΔS_f values were calculated from the heat of fusion values at the melting points[8]).

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Hence growth of naphthalene and benzoic acid should be faceted. The values of heat of fusion obtained from D.S.C. agree with the theoretical values within the error range. Experimental values of $\Delta S_f/R$ were found to be 5.91, 5.17 and 5.49 for naphthalene, benzoic acid and the eutectic, respectively. Higher values of $\Delta S_f/R$ indicate that the eutectic is faceted-faceted type. When the growth of the eutectic was observed in the glass slide under a microscope with suitable magnification, it was seen that the growth was irregular (faceted) in agreement with the recent classification of the eutectics[7]. Not much literature is available on the studies of faceted-faceted eutectics.

(b) *X-ray studies :* From X-ray photographs of the eutectic, naphthalene and benzoic acid, it is clear that there is a marked difference in the interplanar distances and the relative intensities of the composite material and the individual components. From the study of X-ray photographs, the following are evident :

1. A number of X-ray reflections on the X-ray photographs indicate that the eutectic is crystalline in nature.
2. There is a rapid fall in the value of intensity of reflections as a function of the diffraction angle $\frac{\sin\theta}{\lambda}$.

From the study of Table 1, the following characteristic features have been observed. In eutectic, the reflections with interplanar spacing d = 3.65, 3.42, 2.93, 2.52 and 2.27Å have relatively stronger intensities as compared to the similar lines found in benzoic acid and naphthalene. From the above observation, it is inferred that the X-ray diffraction pattern of the eutectic is different from that of the individual components constituting it. In other words, the X-ray photographs of the pure components cannot be exactly superimposed on the photographs of the eutectic composite. Some of the reflections as mentioned above show deviations in the intensity and in interplanar spacings.

It can be inferred from these observations that the eutectic is not only a pure mechanical mixture of two components, but there is orientation of some atomic planes in the composite. Such an observation has also been made by ir studies[6].

The rapid fall in the intensity of reflections can be attributed to various reasons. There may be some disorder in the location of atoms forming the composite. It can also be due to thermal vibration of atoms making the composite. It is the thermal activation of the interaction of the two components which is responsible for the formation of the eutectic. As a confirmation of this effect it is found that reflections are slightly diffused in intensity.

TABLE 1

Naphthalene		Eutectic		Benzoic acid	
d/Å	R.I.	d/Å	R.I.	d/Å	R.I.
—	—	10.84	s	10.90	s
7.28	m	7.28	w	—	—
5.78	w	—	—	—	—
5.62	w	—	—	—	—
—	—	5.42	w	5.48	m
—	—	5.12	vs	5.15	vs
4.65	m	—	—	—	—
—	—	4.68	w	4.68	mw
4.50	vs	4.50	w	—	—
4.12	m	4 18	w	—	—
4.11	w	4.10	w	—	—
3.70	vw	3.71	s	3.71	s
3.64	vw	3.65	s	—	—
—	—	—	—	3.62	w
—	—	—	—	3.50	w
3.51	vw	—	—	—	—
3.48	w	3.48	w	—	—
—	—	3.42	vs	3.42	s
3.38	mw	3.38	m	—	—
3.21	w	3.19	s	3.19	m
3.00	w	2.99	w	—	—
—	—	2.93	s	2.95	mw
2.80	vw	—	—	—	—
2.76	vw	—	—	—	—
—	—	—	—	2.72	vw
—	—	2.56	vw	2.56	vw
2.55	vw	2.52	mw	—	—
2.48	vw	2.48	vw	—	—
—	—	2.42	vw	—	—
2.28	vw	2 27	mw	—	—
—	—	2.09	mw	2.09	vw
1.84	w	1.90	mw	1.91	vw
1.82	w	—	—	—	—
1.81	w	—	—	—	—
—	—	1.61	vw	—	—
—	—	1.58	vw	—	—

The classification of the relative intensity of lines is based on the following criteria : vs = 80-100 , s = 60-80 , m = 40-60 , mw = 20-40 , w = 10-20 and vw = 0-10

It can thus be concluded that X-ray studies indicate a sort of preferential ordering of atoms making an eutectic.

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Transformations of β-Pinene over Platinum-Alumina Catalyst. Part—I : Influence of Contact Time, Temperature and Platinum Concentration

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The catalytic transformations of β-pinene have been investigated over platinum-alumina dual function catalyst containing varying amounts of platinum in the temperature range 200 to 400°. In addition, the influence of contact time on the rate and distribution of products has been studied over 0.6% platinum-alumina at 300°. The performance of the catalyst remains unchanged by its pretreatment either in hydrogen or in oxygen prior to catalytic run. The dehydrogenation activity of the catalyst increases upto 350° beyond which it declines.

β-Pinene isomerizes via two parallel paths . one giving rise to bi- and tricyclic products such as camphene, α-pinene, bornylene and tricyclene and the other giving monocyclic compounds such as dipentene, terpinolene, α- and γ-terpinenes. The terpinenes have been identified as the immediate precursors of cymene. Apart from this, the terpinenes undergo disproportionation to menthenes and menthanes. At higher values of contact time and temperature, menthenes and menthanes get dehydrogenated to cymenes.

Increase of platinum concentration inhibits both isomerization and dehydrogenation activities of the catalyst. *This decrease is ascribed to reduction of the acid sites* and enhancement of platinum crystallite size. Disproportionation reaction is favoured by strong acid sites and small well dispersed platinum crystallites.

β-Pinene is a bicyclic mono-olefinic monoterpene present together with α-pinene in the majority of essential oils derived from coniferae[1]. The first quality Indian turpentine oil contains about 10% β-pinene, 40% α-pinene and 50% 3-carene[2]. These hydrocarbons undergo skeletal isomerization initially due to the cleavage of cyclobutane and cyclopropane rings followed by dehydrogenation and disproportionation reactions over dual function catalysts such as chromia and chromia-alumina catalysts[3-5].

Platinum-alumina, another important bifunctional catalyst, is being increasingly employed in reforming processes as it is found to have enhanced sustained activity and high selectivity. Hence platinum-alumina catalyst was chosen for this work. Further, a survey of literature reveals that a systematic investigation of the transformation of β-pinene over this catalyst in the vapour phase has not so far been reported. The influence of contact time, platinum concentration and temperature on the rate and distribution of products of β-pinene was therefore studied and the results are presented in this paper.

Experimental

Preparation of catalysts :

Alumina (catalyst A) : Alumina was prepared according to the method of Pines *et al*[6].

Platinum-alumina (catalysts B, C, D and E) : The catalysts B, C, D and E were prepared by adding calculated volumes of chloroplatinic acid in water to four weighed samples of alumina to give respectively 0.3, 0.6, 0.9 and 1.4% platinum by weight (confirmed by spectrophotometric analysis[7]). The slurry was stirred for 3 hr and dried at 120° for 24 hr. The temperature was raised slowly while passing pure dry hydrogen to reach 500° in a period of 2 hr and maintained at this for 8 hr. The activated material was powdered and pelletized to 4×4 mm size pellets.

TABLE 1—NOMENCLATURE OF THE CATALYST

Catalyst	Composition
A	Alumina (from aluminium isopropoxide)
B	Platinum-alumina (0.3% Pt)
C	Platinum-alumina (0.6% Pt)
D	Platinum-alumina (0.9% Pt)
E	Platinum-alumina (1.4% Pt)

β-Pinene : Since β-pinene (b.p. 165°) constitutes only 10% of first quality Indian turpentine oil and also it boils very close to 3-carene (b.p. 169°), the separation of this component by fractional distillation was not successful. Hence it was obtained from "Fluka" and its purity was checked by gas chromatography.

Apparatus and procedure : Initial experiments conducted both over oxidised and reduced catalysts did not show any significant variation in the product distribution as indicated in Table 3. Subsequent runs were, therefore, conducted over oxidised catalyst. Other details of the apparatus and experimental procedure have been described in the earlier publications[8-10]. The evolution of molecular hydrogen during this investigation was small due to side reactions. Hence the gaseous products were not considered for computing the *p*-cymene yield.

Surface area : The surface area measurements of catalysts C, D and E were made according to BET method, by adsorption of nitrogen at liquid nitrogen temperature. The experimental procedure and calculations were the same as described by Emmett[11]. The values are found to be 121.1, 171.7 and 230.7 m^2/g respectively. The platinum metal area for the above three catalysts are found to be 30.5, 48.4 and 58.5 m^2/g of catalyst respectively by carbon monoxide adsorption, according to procedure described by Dorling[12].

Results and Discussion

(a) *Contact time :* In order to determine the transformation sequence of β-pinene, the influence of contact time W/F (where W is the weight of catalyst and F is the weight of β-pinene passed per hr over the catalyst) on the product distribution has been studied at 300° over catalyst C (0.6% Pt) and the results are plotted in Fig. 1, while the overall conversion is summarised in Table 2. The distribution of products varied to different extents with increasing contact time (Fig. 1). The various compounds formed are identified to be α-pinene, dipentene, terpinolene, α- and γ-terpinenes, camphene, tricyclene, bornylene, 1-, 3- and 4(8)-*p*-menthenes, *cis*- and *trans*-menthanes and *p*-cymene.

Fig. 1. Effect of contact time on product distribution.

TABLE 2—EFFECT OF CONTACT TIME, PLATINUM CONCENTRATION AND TEMPERATURE ON THE OVERALL CONVERSION OF β-PINENE

Contact Time (hr)	% conversion of β-pinene	% platinum concentration	% conversion of β-pinene	Temperature (°C)	% conversion of β-pinene
0.12	84.0	0.3	98.7	250	98.3
0.4	92.0	0.6	98.8	300	98.8
0.79	98.8	0.9	98.9	350	98.8
1.2	99.0	1.4	98.6	400	97.8
1.6	99.5				

The concentration of individual menthadienes, menthenes and menthanes were too small and varied widely with contact time ; hence they were grouped as menthadienes, menthenes and menthanes. The concentration of *p*-cymene continues to increase with increase in contact time. It can be inferred from this that *p*-cymene is the final product in the transformation of β-pinene and the rest are only intermediates, though formed through different routes (Scheme) and exhibit their maxima at different contact times. Further, it has been observed experimentally that *p*-cymene undergoes neither side chain dehydrogenation nor ring hydrogenation under the experimental conditions. This lends support to the above view regarding the nature of *p*-cymene.

Bornylene and tricyclene register an increase upto 1.2 hr ; thereafter their concentrations remain almost constant. This may be due to the establishment of dynamic equilibrium among tricyclene, bornylene and camphene. Camphene formed by the skeletal isomerization of α- and β-pinenes suffers further skeletal isomerization to monocyclic menthadienes at higher contact time and at higher temperature.

The concentrations of α- and γ-terpinenes were less than the concentrations of dipentene and terpinolene at all contact times studied (Fig. 2). The reason for the low concentration of terpinenes could be the faster rate with which they undergo dehydrogenation as soon as they are formed from dipentene and terpinolene. This observation reveals that terpinenes are the immediate precursors of *p*-cymene.

Menthanes also undergo dehydrogenation like menthadienes but this occurs at higher contact time. Thus the maxima for menthadienes and menthanes occur around 0.12 and 0.79 hr respectively. On the basis of their dehydrogenation to cymenes, menthanes cannot be designated as intermediates like menthadienes since they are formed by disproportionation of menthadienes

DISPROPORTIONATION
MENTHADIENES → MENTHENES + MENTHANES + p-CYMENE
COKE

SCHEME

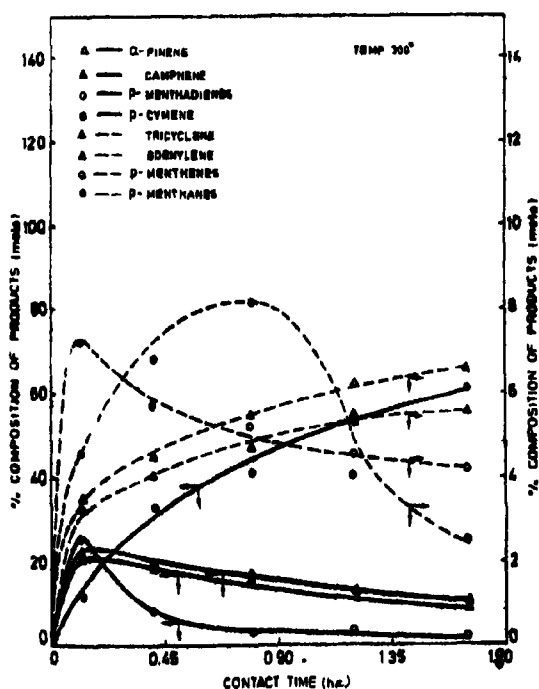
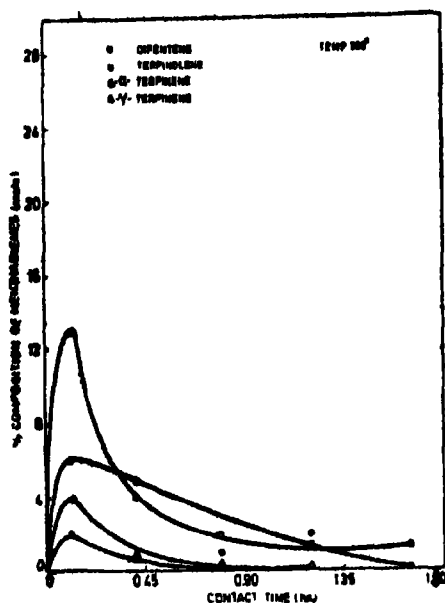
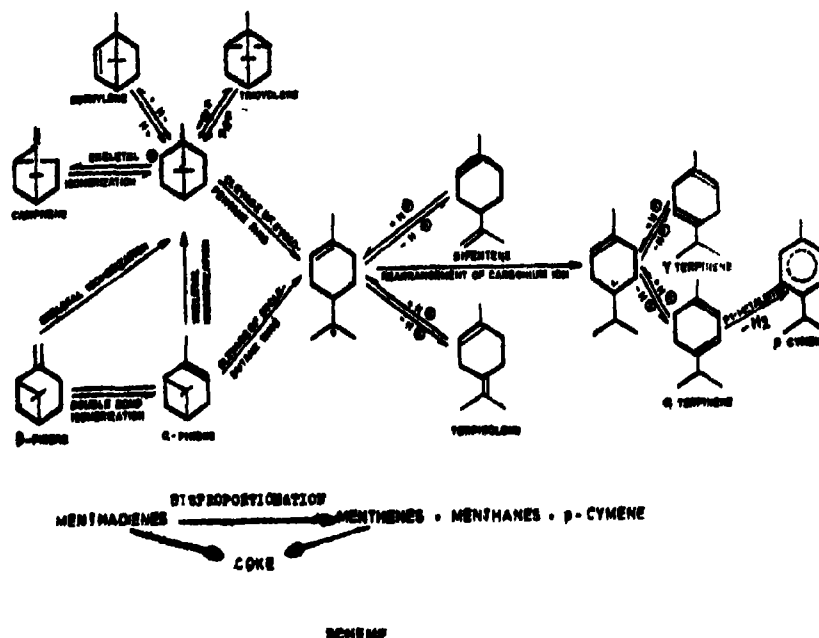
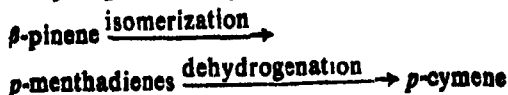



Fig. 2. Effect of contact time on the percentage composition of menthadienes.

which is only a side reaction, not forming part of the dehydrogenation sequence of β-pinene :

$$\beta\text{-pinene} \xrightarrow{\text{isomerization}}$$

$$p\text{-menthadienes} \xrightarrow{\text{dehydrogenation}} p\text{-cymene}$$

However, they can be described as 'pseudo intermediates' which seems to be precise nomenclature on account of their increasing concentration to a maximum followed by a decrease.

Menthenes can either be formed by partial hydrogenation of menthadienes or by partial dehydrogenation of menthanes or by disproportionation of menthadienes. The first possibility is highly unlikely under this condition. Pines *et al*[18] reported that dehydrogenation of menthanes to cymenes over platinum-alumina occurred without the intermediate formation of menthenes and menthadienes. Menthenes are therefore considered to be the disproportionation products of menthadienes as shown below :

$$\text{Menthadienes} \xrightarrow{\text{disproportionation}} \text{Menthenes} + \text{Menthanes} + \text{Cymene}$$

From these observations, the sequence of reactions pertaining to the formation of various products from β-pinene is shown in the Scheme.

(b) *Platinum concentration :* In Table 2 and in Fig. 3 are given the influence of platinum concentrations on the overall conversion of β-pinene and the distribution of products respectively at 300° and at a contact time of 0.79 hr. There is no variation in the overall conversion of β-pinene with increasing platinum concentration as it has reacted almost completely even at 0.3% platinum concentration, showing that β-pinene is highly reactive. On the other hand the various species present in the catalysate are influenced to varying degrees by increased platinum additions. For instance, the proportions of α-pinene and camphene increase while those of tricyclene and menthene decrease. *p*-Cymene and menthanes, after registering their maxima over 0.9% and 0.6% platinum respectively, begin to fall. Bornylene increases to a maximum whereas menthadienes decrease to a minimum, thereafter the former and the latter register decreasing and increasing trends respectively (Fig. 3).

α-Pinene and camphene, formed initially from β-pinene, may not be able to undergo further

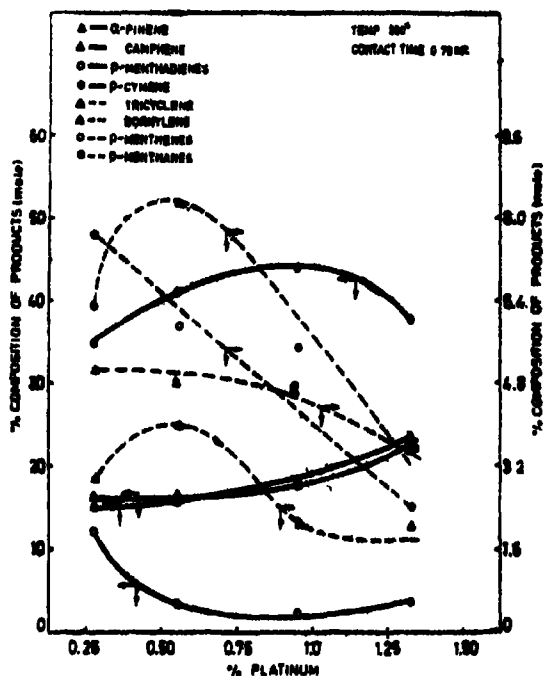



Fig. 3. Effect of platinum concentration on product distribution.

skeletal isomerization due to decrease of the acidic sites of alumina by deposition of platinum metal and hence their concentration in the catalysate increases. Consequently the concentrations of tricyclene, bornylene, menthenes and menthanes in the catalysate decrease.

Among the transition metals, platinum, being the most effective dehydrogenating element, is expected to show greater activity for dehydrogenation reaction when its content in the catalyst increases. But actually a decrease in its activity is observed. Platinum metal area of catalysts C, D and E are 30.5, 48.4 and 58.5 m^2/g of catalyst (and not per gram of platinum). Though the surface area registers an increasing trend, the rate of increase registers a fall in magnitude with increasing platinum concentrations. This is possibly due to a tendency of the platinum crystallites to form clusters at higher concentration. This is reflected by corresponding decrease in the dehydrogenation activity and the increase in concentration of menthadienes. The decrease in the menthane concentration indicates that disproportionation reactions are favoured by both strong acid sites and small well-dispersed metal crystallites. Since at higher platinum concentrations these types of essential sites namely strong acid sites and well dispersed metal sites disappear, a decrease in the concentration of menthanes occurs.

(c) *Temperature* : The effect of temperature on the total conversion of β-pinene and on the distribution of products has been studied over catalyst C at 0.79 hr and the results are presented in Table 2 and Fig. 4, respectively. The catalyst has developed its maximum activity even at 250° with regard to the overall conversion of β-pinene. Temperature beyond 350° has no beneficial effect.

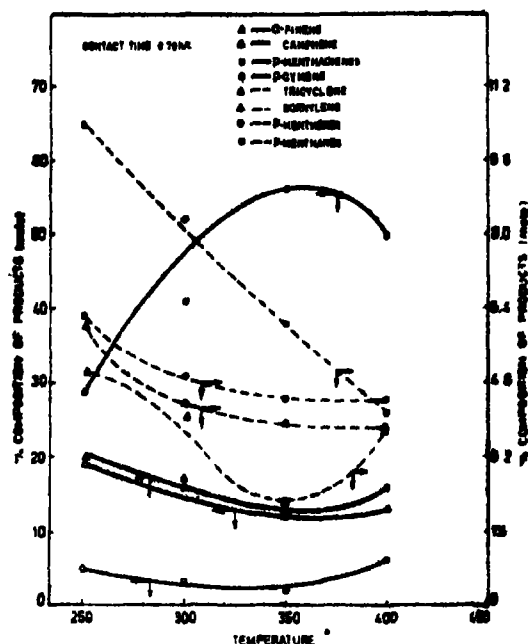



Fig. 4 Effect of temperature on product distribution.

TABLE 3—EFFECT OF CATALYST PRETREATMENT ON THE PRODUCT DISTRIBUTION : D^a=0.9% Pt-Al_2O_3 REDUCED D^b=0.9% Pt-Al_2O_3 NOT REDUCED AFTER REGENERATION ; E^a=1.4% Pt-Al_2O_3 REDUCED AFTER REGENERATION ; E^b=1.4% Pt-Al_2O_3 NOT REDUCED AFTER REGENERATION

Sl. No.	Temp. °C	Contact time (hr)	Catalyst	β-Pinene reacted	α-Pinene	Camphene	Menthadienes	Cymene	Tricyclene	Bornylene	Menthene	Menthane	Carbon estimated
1	250	0.79	D^a	98.8	24.6	19.0	1.6	34.7	5.0	3.8	5.0	6.8	0.56
2			D^b	98.8	20.4	21.5	4.8	34.6	5.0	3.5	4.0	6.2	0.6
1	350	0.79	E^a	98.2	12.8	19.4	2.2	58.7	3.0	2.8	3.0	3.1	0.5
2			E^b	98.7	13.9	20.1	3.2	54.3	3.0	1.3	2.2	2.0	0.6

a=reduced after regeneration.
b=not reduced after regeneration.

In fact a small deactivation of the catalyst was noted around 400°. Temperature around 400° may promote undesired side reactions like cracking and polymerization, leading to the formation of coke which may cause the deactivation of the catalyst.

The proportions of various intermediates, irrespective of their nature, fall rapidly due to their further conversion to the final product, *p*-cymene, which maintains its increasing trend almost linearly upto 350°. Between 350 and 400°, the *p*-cymene formation comes down on account of the deactivation of the catalyst as explained above.

The maximum concentration of menthanes and menthenes occurs around 250° and thereafter their formation registers a decrease From this it is clear that disproportionation reactions are favoured in the lower temperature regions since at higher temperature the species undergoing disproportionation desorb easily before reaction.

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Aza Triterpenes—III† : Action of Excess Hydrazoic Acid-Boron Trifluoride Etherate on 3-Oxo-Penta Cyclic Triterpenes

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3-Oxo-pentacyclic triterpenes (I, II and III) furnished 3-cyano-4-azido-3,4-seco penta cyclic triterpenes (IB, IIB and IIIB) on treatment with excess N_3H-BF_3 etherate both in benzene and chloroform media The reaction did not proceed at 10°. Attempts to build up tetrazole ring system by the action of excess N_3H-conc. H_2SO_4 on 3-oxo-penta cyclic triterpenes(I, II and III) furnished lactams (IA, IIA and IIIA). The lactams were recovered unreacted on treatment with excess N_3H-BF_3 etherate.

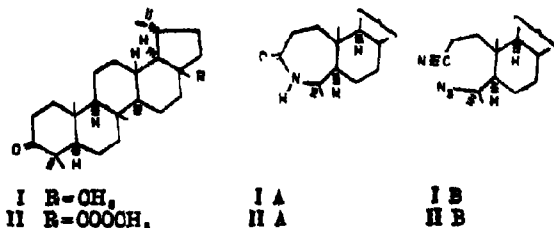
SCHMIDT reaction of ketones with equimolecular quantities of hydrazoic acid yields amides and with excess of hydrazoic acid tetrazoles. Tetrazoles are known to possess biological activity and some are of clinical significance. The tetrazole obtained from cyclohexanone, commercially known as metrazole or cardiazole, is a heart stimulant[1,2]. Steroidal tetrazoles are claimed to possess anti-fertility and anti-spermatogenic activity[3,4].

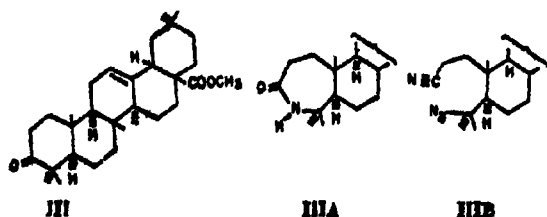
A search in literature revealed that Schmidt reaction with excess of hydrazoic acid-boron trifluoride etherate on triterpene ketones has not been studied. In the present investigation lupenone (I), methyl betulonate (II) and methyl oleanonate (III) were treated with excess hydrazoic acid in presence of freshly distilled boron trifluoride etherate in benzene and chloroform media for 16 hr and 3 hr at room temperature. The reaction products in all the above three cases did not show characteristic absorption for tetrazole ring system in their ir spectra. The ir spectra were also lacking in 7-membered lactam carbonyl absorption, indicating that the reaction did not proceed to give either the tetrazole ring system or the normal Schmidt reaction product. Instead, the ir spectra of the reaction products showed absorption around 2250 cm^{-1} and 2050 cm^{-1}, characteristic of nitrile and azide groups, respectively. This is possible only when there is cleavage in ring A of these triterpene ketones.

The ring fission in the presence of excess hydrazoic acid-boron trifluoride etherate is not uncommon though not a usual feature. The 17-oxo steroids, esteron methyl ether[5] and 4-androstene-3,17-dione[6,7], gave besides tetrazoles, 13, 17-seco-13α-azido-17-nitriles. 5α-Hydroxy-6-oxo-5α-cholestan[8] furnished 3β-acetoxy-5-oxo-5,6-seco cholestan-6-nitrile. On the basis of formation of lactams (IA, IIA and IIIA) in the normal Schmidt reaction of these triterpene ketones (I, II and III)[9], ir spectra and analytical data, 3-cyano-4-azido-3,4-seco structures were assigned to the reaction products (IB, IIB and IIIB). The cleavage of C_3-C_4 bond in this reaction is in conformation with the results of Beckmann rearrangement[9] of the oximes of lupenone, methyl betulonate and methyl oleanonate. These triterpenes have a gem-dimethyl group adjacent to 6-membered keto function. As in the case of Beckmann rearrangement, even in the present instance the gem-dimethyl group next to oxo function is responsible for the cleavage of C_3-C_4 bond. The signal at δ 2.5 (2H) in the nmr spectrum of IB can be assigned to $-CH_2-C{\equiv}N$ supporting the 3-cyano-4-azido-3, 4-seco structure

In an attempt to build up the tetrazole ring system the reaction was conducted at 10° but the compounds were recovered unreacted both in benzene and chloroform media. The 3-oxo-pentacyclic triterpenes (I, II and III) furnished normal Schmidt reaction products (IA, IIA and IIIA) with excess of hydrazoic acid-conc. sulphuric acid both in benzene and chloroform media. For the formation of tetrazoles or the lactams, imido carbonium ion is the intermediate[10] which reacts with water present in sulphuric acid in preference to hydrazoic acid. Treatment of the lactams (IA, IIA and IIIA) with excess of hydrazoic acid-boron trifluoride etherate both in benzene and chloroform media proved unsuccessful in building the tetrazole ring system probably the lactam, once formed, is stable enough not to revert to imido carbonium ion which is a precursor for the formation of tetrazoles.

I R=CH_3 | IA | IB

II R=$COOCH_3$ | IIA | IIB

† Part of the work has presented at the Annual Convention of Chemists, 1979 at Kurukshetra.

III IIIA IIIB

Experimental

Melting points are uncorrected. All the compounds showed consistent elemental analysis. IR spectra were recorded on Perkin-Elmer spectrophotometer in KBr.

1. *Preparation of hydrazoic acid in benzene and chloroform media* : A stirred solution of sodium azide (100 g) in water (250 ml) was cooled to 5-10° and benzene or chloroform (1 l) was added followed by drop-wise addition of conc. sulphuric acid (93 ml) during 30 min at 5-10°. The mixture was stirred for 30 min with temperature kept below 10°. The organic layer was separated and dried.

2. *Action of excess hydrazoic acid-boron trifluoride etherate on 3-oxo-pentacyclic-triterpenes* (I, II, III) *in benzene at room temperature : Isolation of 3-cyano-4-azido-3,4-seco pentacyclic triterpenes* (IB, IIB *and* IIIB) : A typical experiment is described. To 3-oxo-pentacyclic triterpene (1.5 g) in benzene (100 ml), freshly distilled boron trifluoride etherate (10 ml) and hydrazoic acid solution in benzene (200 ml) were added and the mixture kept for 16 hr at room temperature (30-35°). Crushed ice was added to the reaction mixture and the organic layer was washed with ice-cold water. The benzene layer was dried and evaporated. The residue was adsorbed over a column of neutral alumina (50 g) and eluted with benzene (500 ml) and chloroform (500 ml). The benzene eluate gave 3-cyano-4-azido-3,4-seco pentacyclic triterpene (750 mg), crystallising from methanol as colourless needles. Chloroform eluate did not yield any residue on removal of the solvent.

The reaction was conducted in chloroform medium at room temperature for 16 hr and 3 hr duration. The reaction product was 3-cyano-4-azido-3,4-seco pentacyclic triterpene, m.p. : IB 220°, IIB 215° and IIIB 215°. IR : IB 2250 cm^{-1} and 2050 cm^{-1} ; IIB 2250 cm^{-1} and 2040 cm^{-1} and IIIB 2235 cm^{-1} and 2045 cm^{-1} for $-CN$ and N_3 groups, respectively. NMR for IB δ 2.5(2H for $-CH_2-C\equiv N$).

3. *Action of excess hydrazoic acid on 3-oxo-pentacyclic triterpene in presence of conc. sulphuric acid in benzene : Isolation of 3-oxo-3a-aza-A-homo pentacyclic triterpenes* (IA, IIA and IIIA) : A typical experiment is described. To 3-oxo-pentacyclic triterpene (1.5 g) in benzene (100 ml), conc. sulphuric acid (3 ml) and hydrazoic acid in benzene (200 ml) were added and kept for 16 hr at room temperature (30-35°). Crushed ice was added to the reaction mixture and the organic layer was washed with ice-cold water. The benzene layer was dried and evaporated. The residue (900 mg) was adsorbed over a column of neutral alumina (50 g) and eluted with benzene (500 ml) and chloroform (500 ml). The benzene eluate did not yield any residue on removal of the solvent. Chloroform eluate yielded 3-oxo-3a-aza-A-homo pentacyclic triterpene, identical with the product obtained in the Schmidt reaction of 3-oxo-pentacyclic triterpene[9], m.p. : IA 258° ; IIA 256° ; IIIA 258° (lit[9] m.p.s 258, 256 and 258 for IA, IIA and IIIA, respectively).

IR : IA 3230 cm^{-1} and 1675 cm^{-1} ; IIA 3225 cm^{-1} and 1675 cm^{-1} ; IIIA 3220 cm^{-1} and 1675 cm^{-1} for NH and $-CONH$ respectively. NMR IIIA δ 5.5 (H) exchangeable with D_2O for NH.

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Synthesis of 3-Heteraryl Coumarins as Optical Brighteners

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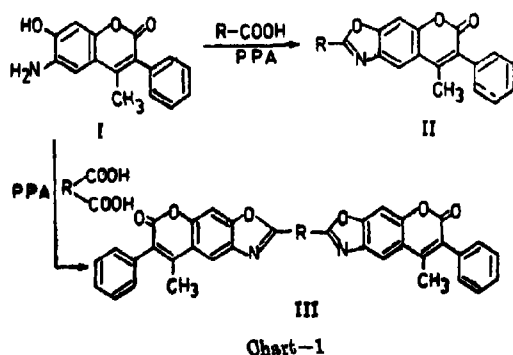
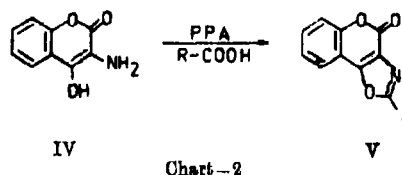
A few 2-aryl and 2-heterocyclic substituted (6,7) coumarinoxazoles have been synthesised by condensing 6-amino-7-hydroxy-3-phenyl-4-methylcoumarin with aromatic and heterocyclic carboxylic acids with the aid of polyphosphoric acid. The ultraviolet, infrared, nmr, mass and fluorescence spectra of these compounds have been presented for characterisation.

7-(2'-Benzoxazolyl)-3-phenylcoumarins[1] and 2-(3'-coumarinyl) benzoxazoles[2] have been reported to be optical brighteners for polyesters, polyamides and polyvinyl chloride. 2-(3'-Coumarinyl) naphthoxazoles with a dialkylamino substituent in 7-position of the coumarin ring exhibit brilliant fluorescence with absorption in the visible range and are useful for the dyeing of organic fibres[3]. Coumarin derivatives, specially 3-aryl-7-substituted aminocoumarins, because of their intense blue fluorescence and good light fastness constitute an important group of optical brighteners for synthetic fibres like polyamide and polyester[4]. In our earlier studies[5] coumarino-oxazoles with aromatic or heterocyclic substitution in 2-position have been found to possess high fluorescence in uv and visible region. Encouraged by these results, in our present investigation, various 2-(3-coumarinyl)-4'-methyl-3'-phenylcoumarino-(6',7' : 4,5) oxazoles, 2-(3-aryl, 3-naphthyl, 3-heteraryl) oxazoles and *bis* oxazoles have been synthesized by the condensation of 4-methyl-3-phenyl-6-amino-7-hydroxycoumarin (I) with various substituted coumarin-3-carboxylic acids, aromatic carboxylic acids, naphthoic acids, pyridine carboxylic acids and dicarboxylic acids to get the corresponding oxazoles II, III using polyphosphoric acid as the cyclodehydrating agent.

Chart—1

In addition to the above compounds a few 2-(3'-coumarinyl)-coumarin (3 : 4) oxazoles have been synthesized to study the effect on fluorescence of oxazole moiety on the pyrone part of the coumarin. For the purpose of synthesizing the above compounds 3-amino-4-hydroxycoumarin (IV) was condensed with various coumarin-3-carboxylic acids to get the corresponding oxazoles (V) using polyphosphoric acid as cyclodehydrating agent.

Chart—2

The above compounds have been characterized by uv, ir, nmr, mass and fluorescence spectral data.

UV spectra : The uv spectra of all the compounds were recorded on Beckmann DK 2A spectrophotometer using dioxane as solvent. All the title compounds exhibited three main regions of absorption around 368 ± 30, 283 ± 5 and 253 ± 10 nm. The fluorescence spectra for all the compounds were measured on Beckmann DK 2A spectrophotometer using dioxane as the solvent. The results are tabulated in Tables 1A, 1B and 1C.

The information obtained from the fluorescence spectrum may be used in the evaluation of the compounds as possible fluorescent brighteners for synthetic fibres, plastics, papers etc. An ideal fluorescent brightener should absorb in the uv region between 340 and 400 nm and emit in the visible region[6]. The maximum of these resulting

TABLE 1A

Sl. No.	2-(Heteraryl)-4'-methyl-3'-phenylcoumarino-(6',7' : 4,5) oxazole	max. absorption nm	max. emission nm	Difference	Colour observed
1.	2-(3-Coumarinyl)-	369	455	86	Blue
2	2-(6-Methyl-3-coumarinyl)-	371	457	86	Blue
3.	2-(8-Methyl-3-coumarinyl)-	369	456	87	Blue
4.	2-(6-Bromo-3-coumarinyl)-	370	469	99	Blue
5.	2-(5,6-Benzo-3-coumarinyl)-	396	483	87	Green
6.	2-(2-Naphthyl)-	359	400	41	Violet
7.	2-(p-Toluyl)-	342	426	84	Violet
8.	2-(1-Naphthyl)-	369	406	37	Violet
9.	2-(Benzyl)-	329	430	101	Light violet
10.	2-(3-Pyridyl)-	354	408	54	Light violet
11.	2-(4-Pyridyl)-	353.5	410	56.5	Light violet

TABLE 1B

Sl. No.	Name of the compound	max. absorption	max. emission	Difference	Colour observed
1.	*Bis*-[4'-methyl-3'-phenyl-coumarino-(6',7' : 4,5)-oxazolo] methane	326	437	111	Light violet
2.	*Bis*-[4'-methyl-3'-phenyl-coumarino (6',7' : 4,5) oxazolo] ethylene	408.5	456	47.5	Blue
3.	*Bis*-1,4-[4'-methyl-3'-phenyl-coumarino (6',7' : 4,5)-oxazolo] benzene	398	478	105	Green

TABLE 1C

Sl. No.	2-(3-Heteraryl)-coumarino(3',4' : 4,5) oxazole	max. absorption	max. emission	Difference	Colour observed
		nm	nm		
1.	2-(3-Coumarinyl)-	355	455	100	Blue
2.	2-(8-Methyl-3-coumarinyl)-	365	457	92	Blue
3.	2-(5,6-Benzo-3-coumarinyl)-	393	478	115	Green

fluorescent light, which determines the colour ranges, is between 415-465 nm. The fluorescent maxima of all the 2-(3-coumarinyl)-coumarino oxazoles have emission in the ideal range and therefore these compounds are potential optical brighteners.

IR spectra : The ir spectra of the compounds have been recorded on Perkin Elmer Model 137 in KBr. All the coumarino-oxazoles exhibited a strong band around 1730 ± 15 cm^{-1} characteristic of coumarin carbonyl group. In addition, peaks at 1550 to 1570 cm^{-1}, 1100 ± 15 cm^{-1}, 1360 ± 10 cm^{-1}, attributable to $>C=N$, $-C-O-C-$ and $>C-N=$ of the oxazole system, respectively, have also been found to be common.

NMR spectra : The nmr spectra were recorded on Varian A-60 nmr spectrophotometer in DMSO and $CDCl_3$. The details of the spectra are given in Table 2.

TABLE 2—2-(8-METHYL-3-COUMARINYL)-4'-METHYL-3'-PHENYLCOUMARINO-(6',7' : 4,5) OXAZOLE

δ values	No. of protons	Assignment
2.45 (s)	3	8 Methyl protons
2.55 (s)	3	4' Methyl protons
7.33-7.55(m)	10	Aromatic protons
8.25(s)	1	Vinyl proton

Mass spectra : The mass spectra was recorded on RMU-6L Mass spectrometer with inlet temperature ranging from 150 to 200° and an electron beam energy of 70 ev. The mass spectrum of 2-(8-methyl-3-coumarinyl)-4'-methyl-3'-phenyl-coumarino-(6', 7' : 4, 5) oxazole has been recorded. The molecular ion peak at m/z 435 is the base peak. The peaks at m/z (% abundance) 407 (95%), 379 (22%), 105 (70%) and 64 (38%) are observed in the mass spectrum of the above compound. The major fragmentation mode is loss of carbon monoxide as observed in the case of simple coumarins[7].

Experimental

Preparation of 6-amino-7-hydroxy-3-phenyl-4-methylcoumarin : Synthesized from 5-nitroresacetophenone as reported earlier[8] but with certain modifications in the process of deacetylation and reduction.

5-Nitroresacetophenone (5 g), sodium phenyl acetate (10 g) and acetic anhydride (60 ml) were mixed together and refluxed in an oil bath at 180° for 8 hr. The reaction mixture on pouring in ice water, filtration and recrystallisation from acetic acid yielded 6-nitro-7-acetoxy-3-phenyl-4-methylcoumarin, m.p. 201°. 2 g of the above compound was added to 50 ml of 5% sodium carbonate solution and refluxed for 3 hr. On neutralisation, it gave 6-nitro-7-hydroxy-3-phenyl-4-methylcoumarin, m.p. 223°.

2.7 g of the above nitro compound was mixed with 7 g sodium dithionite, 30 ml ammonia, 30 ml water and 15 ml rectified spirit, refluxed for 15 min and cooled. The compound separated on recrystallisation gave 6-amino-7-hydroxy-3-phenyl-4-methylcoumarin, m.p. 240°.

Preparation of 2-(3-coumarinyl, aryl, heteraryl, naphthyl)-4'-methyl-3'-phenylcoumarino-(6', 7' : 4, 5) oxazoles : Polyphosphoric acid was prepared by stirring a mixture of phosphorous pentoxide (15 g) and orthophosphoric acid (10 ml) at 100° for 1 hr. A mixture of 6-amino-7-hydroxy-3-phenyl-4-methylcoumarin (0.005 mole) and appropriate acid (0.005 mole) was then dropped into the above. The reaction mixture was heated first at 150-60° for 2 hr and then at 200-205° for further 2 hr. The reaction product was poured over ice cold water and the resulting solid was washed with sodium bicarbonate. Recrystallisation was effected with appropriate solvent as shown in Table 3.

Preparation of bis *oxazoles :* The quantity of the 6-amino-7-hydroxy-3-phenyl-4-methylcoumarin taken was (0.01 mole), twice the quantity of the dicarboxylic acid (0.005 mole). The reaction was maintained at 140° for 2 hr and then at 160° for 4 hr. The reaction product was worked out as above.

Preparation of 2-(3-heteraryl)-coumarino-(3', 4', : 4,5)-oxazoles : Polyphosphoric acid was prepared as above and a mixture of 3-amino-4-hydroxycoumarin[9] (0.005 mole) and appropriate acid (0.005 mole) was dropped into it. The reaction mixture was heated first at 150-60° for 2 hr and then at 200-205° for 2 hr. The reaction mixture was poured over ice water and the resulting solid was washed with sodium bicarbonate. Recrystallisation details are included in Tables 3A, 3B and 3C.

TABLE 3A

Sl. No.	2-(Heteraryl)-4'-methyl-3'-phenylcoumarino-(6',7' : 4,5) oxazole	m.p. °C	Yield %	Solvent of recrystallisation
1.	2-(3-Coumarinyl)-	225	60	Dioxane
2.	2-(6-Methyl-3-coumarinyl)	275	60	Dioxane
3.	2-(8-Methyl-3-coumarinyl)-	356	60	Dioxane
4.	2-(6-Bromo-3-coumarinyl)-	330	60	Dioxane
5.	2-(5,6-Benzo-3-coumarinyl)-	315	40	Dioxane
6.	2-(2-Naphthyl)-	325	70	Benzene
7.	2-(1-Naphthyl)-	308	60	Benzene
8.	2-(p-Toluyl)-	280	75	Benzene
9.	2-(Benzyl)-	288	50	Benzene
10.	1-(3-Pyridyl)-	325	60	Benzene
11.	2-(4-Pyridyl)-	320	60	Benzene
12.	2-(o-toluyl)-	263	75	Benzene

TABLE 3B

Sl. No.	Name of the compound	m.p °C	Yield %	Solvent of recrystallisation
1.	*Bis*-[4'-methyl-3'-phenyl-coumarino-(6',7' : 4,5)-oxazolo] methane	268	40	Dioxane
2.	*Bis* [4'-methyl-3'-phenyl-coumarino-(6',7' : 4,5)-oxazolo] ethylene	325	40	Dioxane
3	*Bis*-1,4-[4'-methyl-3'-phenyl-coumarino-(6',7' . 4,5)-oxazolo] benzene	272	60	Dioxane

TABLE 3C

Sl. No.	2-(3-Heteraryl)-coumarino-(3',4' : 4,5) oxazole	m.p. °C	Yield %	Solvent of recrystallisation
1.	2-(3-Coumarinyl)-	273	50	Dioxane
2.	2-(5,6-benzo-3-coumarinyl)-	290	40	Dioxane
3.	2-(8-Methyl-3-coumarinyl)-	295	50	Dioxane

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Free Acids in Lac Resin

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Lac resin has been found to contain 10.70% free fatty and 2.7% free aldehydic terpenic acids. The free fatty acids are composed of (i) saturated and unsaturated straight, chain lengths of C_{14}, C_{16} and C_{18}, (ii) 6-ketotetradecanoic, (iii) 6 hydroxy-tetradecanoic (butolic), (iv) 16-hydroxyhexadecanoic, (v) 16-hydroxyhexadec-*cis*-9-enoic, (vi) *threo* 9,10-dihydroxy of C_{14} and C_{16} chain lengths and (vii) *threo*-9,10,16-trihydroxy hexadecanoic (aleuritic) acids, while the terpenic acids constitute a mixture of jalaric, *lacci*jalaric and a new aldehydic acid ($C_{15}H_{19}O_{5}$)

STUDIES on the constitution of lac resin[1-5] and its two fractions, the pure[4,16] and the soft[5,6] resins, revealed that at least 18 constituent acids, comprising non-hydroxy and hydroxy fatty acids of C_{14} to C_{18} carbon chains and terpenic acids take part in the resin formation. It is believed that these acids are present in the resin mainly through ester[1] and acylal[7-9] linkages. Some workers[10,11], however, have casually indicated that a few of these acids are free in the resin to some extent. Since the presence of some of the constituent acids in the free state might have some interesting bearing on the resin formation, a systematic study was necessary to arrive at a decisive conclusion. The present paper relates to such an attempt to isolate and identify the free acids present in lac resin.

Isolation of free acids : A 30% solution of dewaxed lac in 95% ethanol was exhaustively extracted with *n*-hexane and 12 fractions collected. TLC examination showed the fractions to contain mainly non-, mono-, di- and tri-hydroxy acids. However, butolic acid (6-hydroxytetradecanoic acid) appeared to be the major component of fractions 4 to 12. The fractions were combined and after removal of the neutral fraction and traces of wax, methylated and then acetylated[12]. The acetylated product was fractionated with urea[13] to give adducted (A) and non-adducted (B) esters. TLC examination on silver nitrate impregnated plates[14] revealed that A consisted of saturated and unsaturated non-hydroxy and ω-acetoxy esters along with keto ester while B of keto esters along with mono-, di- and triacetoxy esters.

Fractionation of A with increasing proportions of ether in light petroleum on a column of silica gel impregnated with silver nitrate[15] afforded the pure components. Similarly, pure constituents from B were separated over a column of silica gel. The pure constituents were identified by adopting various methods as described in the experimental.

In the above investigation, the presence of free aleuritic acid has only been indicated but its exact amount, as well as the presence of jalaric and other aldehydic terpenic acids could not be obtained, although their presence in sufficient amounts was reported earlier[10,11]. This may be due to the fact that these acids are practically insoluble in hexane. The following alternate method was, therefore, tried to achieve their isolation.

Palas seedlac was dissolved in Na_2CO_3 solution, the sodium salts of lac resin salted out with NaCl solution and the neutral fraction separated from the mother liquor. Half of the liquor was treated for estimation of aleuritic acid and the other half for the terpenic acids. TLC of the mother liquor showed that the aldehydic acids were mainly composed of jalaric acid with small amount of *lacci*jalaric acid and a new aldehydic acid recently isolated by Prasad[16]. Table 1 summarises the percentage of the free acids isolated so far from lac resin in the present study.

TABLE 1—PERCENTAGE OF FREE ACIDS

1	Saturated straight , chain lengths of C_{14}, C_{16} and C_{18}	0.30
2	Unsaturated straight chain lengths of C_{14}, C_{16} and C_{18}	0.06
3	6-Ketotetradecanoic	0.45
4	6-Hydroxytetradecanoic	2 37
5	16-Hydroxyhexadecanoic	0.57
6	16-Hydroxyhexadec-*cis*-9-enoic	0 77
7	*Threo*-9,10-dihydroxy of chain lengths C_{14} and C_{16}	1.37
8	*Threo*-9,10,16-trihydroxyhexadecanoic (aleuritic)	4 88
9	Aldehydic terpenic	2.68
	Total	12 40

The results obtained in the present study confirmed the findings of Sengupta[11] who reported the presence of free acids to the tune of 8-10% in lac resin. Though the presence of C_{18} straight chain free acids have been indicated, no indication has been observed for the presence of such hydroxy saturated or unsaturated acids in lac resin.

The unsaturated acids indicated at Sl. Nos 2 and 6 appear to be the precursors of various mono-, di- and tri-hydroxy acids. These free acids as such

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or in loose combination may be considered as the primary building blocks of lac resin. This contention has been further supported by Singh *et al*[6,11], who have succeeded (i) in isolating 4 essentially pure acid esters (jalaric ester—I and II and *lacci*jalaric ester—I and II) constituting the bulk of soft resin, (ii) in synthesising the possible key compounds (jalaric ester – I and *lacci*jalaric ester – I) of lac resin. They have reported that 16-hydroxy hexadec-9-enoic acid seems to play a key role in the elaboration of these compounds by the insect.

Experimental

All m.p.s and b.p.s are uncorrected. Light petroleum refers to the fraction b.p. 40-60. Silica gel for column chromatography was 100-200 mesh. TLC was carried out on silica gel layers (0.3 mm) containing 15% gypsum; visualization agent—iodine vapours or heating at 150°. Mixed solvent composition is by volume. Perkin-Elmer Infracord 700A and AIMIL, Gas-liquid chromatography equipment were used for ir spectral and constituent analyses, respectively.

Dewaxed shellac (100 g), prepared from *Palas* seedlac by the method of Khurana *et al*[4], was dissolved in 95% methanol (300 ml) and exhaustively extracted with 1 litre lots of *n*-hexane in succession. Altogether 12 fractions, totalling 7.06 g, which were 2.98, 1.25, 0.97, 0.63, 0.42, 0.29, 0.27, 0.09, 0.06, 0.05, 0.04 and 0.014 g, respectively, were isolated. The tlc examination of the fractions (solvent system, 2% acetic acid in ethyl acetate) along with authentic samples revealed that all the fractions were mixtures of mainly non-, mono-, di-, tri-hydroxy and keto acids. However, butolic acid was found as the major component in fractions 4 to 12. These fractions were, therefore, mixed together and repeatedly extracted with warm light petroleum. The warm extract yielded a crystalline mass (0.65 g) on cooling which, after recrystallisation from aqueous methanol, melted at 56-57°. The acid was identified as butolic (6-hydroxytetradecanoic) acid on the basis of its tlc (R_f 0.73), mixed m.p. (55-56°), oxidative degradation and ir spectrum 3225 cm^{-1} (OH), 1710 cm^{-1} (COOH).

As the nature of the first 3 fractions and the combined one, left after separation of butolic acid, was similar, they were combined, taken in ether and extracted with 10% Na_2CO_3 solution (100 ml × 4) leaving the wax and neutral portions in the ether. The acidic mass (6.04 g) recovered on acidification of Na_2CO_3 extract, was converted into methyl esters by refluxing with 1% methanolic H_2SO_4 for 4 hr. The methyl esters were then acetylated[12] with acetic anhydride (35 ml) at 100° for 4 hr to yield 6.6 g acetylated esters.

Urea-fractionation[13] *:* The acetoxy esters (6.5 g) were dissolved in methanol (70 ml), urea (12 g) added and warmed to get a clear solution. The solution was allowed to stand at room temperature for 48 hr. The adduct was separated, washed with methanol saturated with urea, decomposed with warm water and extracted with ether yielding adducted acetoxy ester (**A** ; 2.12 g). Similarly, non-adducted acetoxy (**B** ; 4.41 g) was also recovered. TLC of the fractions on silver nitrate impregnated plates[14] indicated **A** to contain saturated and unsaturated non-hydroxy and ω-acetoxy esters along with keto esters [solvent system, light petroleum : ether (80 : 20)] while **B** to contain keto esters along with mono-, di- and tri-acetoxy esters.

Chromatography of adducted esters **A** (2.10 g) :

The fraction **A** was chromatographed in 6 lots on silica gel columns impregnated with silver nitrate[15] (10 g) mixed with hyflosupercel (5 g) and eluting with 100 ml lots of light petroleum-ether mixtures and collecting in 10 ml portions. The fractionation was monitored by tlc on silver nitrate impregnated plates and the corresponding fractions combined, giving finally 6 fractions (A-1 to A-6 ; 2.02 g). The fractions A-1 and A-2 were saturated (R_f 0.65) and unsaturated (R_f 0.46) non-hydroxy esters, respectively while the fractions A-3 and A-5 were saturated (R_f 0.32) and unsaturated (R_f 0.25) ω-acetoxy esters, respectively. Fraction A-4 appeared to be keto ester (R_f 0.61) and A-6 was a mixture of esters Fractions A-1 and A-2 were identified by glc as mixtures of saturated and unsaturated C_{14}, C_{16} and C_{18} ordinary esters respectively on the column of polyethylene glycol adipate (PEGA, 10% w/w) at a column temperature of 200° by running separately with standard esters.

ω-Acetoxy esters

Saturated : The hydroxy acid derived from fraction A-3 was shown to be 16-hydroxy hexadecanoic acid on the basis of the following evidences.

The acid, on crystallisation from ether, melted at 92-93° (lit[17] 91-93°). Mixed m.p. 93-94°; ir (methyl ester, m.p. 52-53°) : 3278 cm^{-1} (OH), 1047 cm^{-1} (primary OH) and 1718 cm^{-1} (ester carboxyl). Oxidation[18] of the acid gave 1,16-hexadecane dioic acid[19], m.p. 118-119°. The chain length determination[20] showed that the ester was mainly C_{16} in its chromatographic behaviour over glc. (Found : C, 70.67 ; H, 11.72. $C_{16}H_{32}O_3$ requires C, 70.59 ; H, 11.76%). (A.V. = 200.7, H.V. = 194.0 and acid equiv. = 279.0).

Unsaturated : The liquid unsaturated hydroxy acid isolated from A-5 was confirmed as 16-hydroxy hexadec-*cis*-9-enoic acid on the basis of its oxidation[21,22] to C_7 and C_9 dibasic acids, hydrogenation to saturated ω-hydroxy acid and ir spectrum. The methyl ester did not show any peak at 968 cm^{-1} corresponding to a *trans* double bond indicating its configuration as *cis*. (Found : C, 70.22 ; H, 10.57. $C_{16}H_{30}O_3$ requires C, 71.11 ; H, 11.11%).

Keto ester (A-4) : The acid recovered from fraction A-4 melted at 70-71° (mixed m.p. 70-71°) was identified as 6-keto tetradecanoic acid on the basis of tlc (methyl ester, R_f 0.61), ir (two peaks at 1737 cm^{-1} and 1718 cm^{-1} corresponding to keto and ester carboxyl groups, respectively), semi carbazone derivative[23] (m.p. 129-130°) and sodium

borohydride reduction to 6-hydroxy tetradecanoate (methyl butolate).

Chromatography of non-adducted esters **B** :

The non-adducted acetoxy esters B (4.4 g) were chromatographed over silica gel into 4 fractions (B-1 to B-4 ; 4.21 g) with increasing proportions of ether in light petroleum. TLC showed B-1, B-2 and B-3 to be 6-ketotetradecanoate (R_f 0.61), acetoxy butolate (R_f 0.42) and diacetoxy ester (R_f 0.28), respectively. B-4 was mainly triacetoxy ester (R_f 0.12). The acids recovered from B-1 and B-2 were identified in usual manner as described earlier.

Diacetoxy ester **B-3** : The acid derived from fraction B-3 formed isopropylidene[24] derivative. The derivative was a liquid which moved as single spot (R_f 0.62). The corresponding R_f value for the derivative of an authentic 9-10-dihydroxy tetradecanoic acid was 0.61 in the solvent system, light petroleum : ether : methanol (50 : 40 : 10). The dihydroxy acid has R_f 0.30 and its methyl ester R_f 0.25. The hydroxy ester behaved in a similar manner as methyl *threo*-isomer on a tlc plate impregnated with boric acid[14] in the solvent system, light petroleum : ether (60 : 40). Chromic acid as well as potassium permanganate and periodate oxidation[21] yielded azelaic acid as one of the oxidation products. The other fission products may presumably be either pentanal or heptanal if the dihydroxy acid is C_{14} or C_{16}. Since either of the two fission products could not be isolated in pure form, it is presumed that the fraction B-3 is probably a mixture of *threo*-9-10-dihydroxy C_{14} and C_{16} acids. The melting point of the acid (m.p. 83-87°) was, however, not sharp.

Triacetoxy ester **B-4** : Fraction B-4 on hydrolysis afforded a trihydroxy acid (0.29 g) which melted at 99-100°. The acid was identified as *threo*-9,10,16-trihydroxyhexadecanoic acid (aleuritic acid) by the established methods.

Isolation of free aldehydic terpenic acids : Powdered *Palas* seedlac (100 g) was dissolved in Na_2CO_3 solution (4%) by warming and diluting the solution to 1 litre with warm water. The cold solution was filtered to remove wax and impurities. The sodium salts of lac resin were then salted out with saturated NaCl solution and allowed to stand overnight. The clear liquor was decanted and the residue washed twice with NaCl solution. The solutions were mixed together and extracted with ether to remove the neutral portion, if any. The liquor portion was then divided into two parts (X) and (Y).

The first part (X) was decomposed with dil. H_2SO_4, impurities filtered and the solution extracted with ethyl acetate. The resinous mass thus obtained was examined by tlc, [solvent system, ethyl acetate : acetic acid (100 : 2)], plate sprayed with 2,4-DNPH solution which revealed it to be a mixture of jalaric (R_f 0.44), *lacci*jalaric (R_f 0.65) and an unknown aldehydic acid (R_f 0.56). The resinous mass was then digested with chloroform and 2 fractions, chloroform-soluble and chloroform-insoluble, were separated.

Chloroform-insoluble fraction : It was gummy in nature. TLC showed it to be a mixture of mainly jalaric and *lacci*jalaric acid (R_f 0.42 and 0.65). It was chromatographed over silica gel eluting with increasing proportion of ethyl acetate in benzene and collecting altogether three fractions. The first fraction (R_f 0.42) was confirmed as jalaric acid by adopting the established procedures. The second fraction was a mixture of jalaric and *lacci*jalaric acids while the third fraction was identified as *lacci*jalaric acid (R_f 0.65).

Chloroform-soluble fraction : It was evaporated to dryness to get a viscous liquid mass which showed a single spot (R_f 0.56) on tlc plate sprayed with 2,4-DNPH reagent. The acid could not be crystallised and hence 2,4-DNPH derivative was prepared which melted at 113-115°. IR : 1740 cm^{-1} (–CHO), 1725 cm^{-1} (–COOH) and 1610, 1590 cm^{-1} (–C=C, absence of –OH group). UV : λ_{max}^{EtOH} 210 nm and ϵ=7,280 (Found : C, 73.18 ; H, 7.30. $C_{15}H_{18}O_3$ requires C, 73.17 ; H, 7.31%). A.V.=228.8, acid equiv.=246. Mol. formula $C_{15}H_{18}O_3$. It appears that the acid does not resemble either jalaric or *lacci*jalaric acid but seems to be a new one. The structure is being studied.

In another lot, the resinous mass containing the mixture of aldehydic acids was treated with excess of aqueous 2,4-DNPH solution. There was immediate separation of yellow precipitate. The mixture was heated and allowed to stand overnight. The precipitate was filtered and repeatedly washed with dil. HCl. The derivative, on recrystallisation from absolute MeOH, melted at 204-207° with decomposition. The weight of the pure derivative was 4.4 g which amounts to 2.68 g of aldehydic acids on the basis of jalaric acid, the major component.

Isolation of free aleuritic acid : The second part (Y) of the mother-liquor was made just acidic with dil. H_2SO_4 and extracted with *n*-butanol. The extract was dried over anhydrous Na_2SO_4, distilled and finally evaporated to dryness to get a viscous compound (0.47 g from 200 ml mother liquor). TLC showed it to be a mixture of 2 components (R_f 0.22 and 0.79) indicating one of the components as aleuritic acid [R_f 0.21 in the solvent system ethyl acetate – acetic acid (100 : 2)]. The amount of aleuritic acid in this compound was estimated by adopting the method of Sengupta[26] and found to be 4.83%.

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Paper Electrophoretic Separation and Estimation of the Constituents of Pyrolusite and Indian Coin (Cupro-nickel)†

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The separation of the main constituents of pyrolusite and Indian coin paper electrophoretically under a potential gradient of 2.2 volts/cm using 0.1 *M* sodium acetate and 0.1 *M* sodium formate as carrier electrolyte on Whatman Paper No 1 (3 cm × 40 cm) shows that iron and manganese from pyrolusite and copper and nickel from cupro-nickel Indian coin can be successfully separated and determined spectrophotometrically after eluting from the paper. Advantage of this method over existing methods is that separation is possible in 15 min.

SUCCESSFUL separations[1-4] of Fe(III) from Co(II), Mn(II) and Ni(II); Pb(II) from Co(II) and Mn(II); Bi(III) from Co(II) and Mn(II); Hg(II) from Cu(II), Mn(II) and Co(II); and Cu(II) from Co(II) using 0.1 *M* sodium acetate solution as supporting electrolyte, and Cu(II) from Mn(II), Co(II), Ni(II); Fe(III) from Co(II), Ni(II), Mn(II) using 0.1 *M* sodium formate solution as supporting electrolyte by paper electrophoresis have been achieved. This prompted us to attempt an analysis of pyrolusite and Indian coin (cupro-nickel) by paper electrophoresis and a subsequent estimation of Fe, Mn and Cu, Ni.

Ore analysis :

Preparation of migrant solution (pyrolusite)[5-8] *:* Pyrolusite (0.4987 g) was decomposed by 15 ml conc. HCl by evaporating to almost dryness. 15 ml dil. HCl (1 : 1) was added, heated to dissolve the residue and evaporated. The soluble residue was dissolved in minimum amount of dil. HCl. The solution was filtered in a 50 ml volumetric flask. The volume of the solution was made up with dil. HCl.

Paper electrophoresis of the migrant : A drop of pyrolusite solution (1.2×10^{-4} g) having iron and manganese as the main constituents was electrophorised using 0.1 *N* sodium acetate as the supporting electrolyte. Apparatus used for the separation of iron and manganese of pyrolusite was a Durrum's type vertical electrophoretic instrument. Paper strips (3 cm × 40 cm) from Whatman No. 1 were used as the supporting medium, 800 volt applied and the paper strip was taken out after 15 min run and dried. The zones of the migrants were identified with the help of specific reagent, potassium ferrocyanide for iron and 3 *N* potassium hydroxide solution for manganese.

It was found that clean separation of iron and manganese was possible. Separation sequences and position of migrating zone from the point of application after 15 min run is shown in Table 1, where '+' sign indicates migration towards the anode and '−' sign towards the cathode.

TABLE 1—CARRIER ELECTROLYTE 0.1 *N* SODIUM ACETATE

Migrant	Separation sequences of the migrant and the distance traversed by the zone in cm	
	Iron	Manganese
Pyrolusite	+0.9 to −0.3	−1.9 to −2.7

Estimation of iron and manganese : After electrophoresis, the electrophoregram was dried and the portions of the strip containing iron and manganese were cut out from it after matching the said portions against the stained marked strip

Iron (direct method) : The region of the strip containing iron was treated with 2 *N* HCl and evaporated almost to dryness. The residue was treated with 0.8 *N* H_2SO_4, warmed and filtered into a 25 ml measuring flask. A little of 0.8 *N* H_2SO_4 was added and washings of the strips were poured into the measuring flask. The volume was made up to the mark with 0.8 *N* H_2SO_4.

A blank solution was prepared taking the same paper strip of identical dimension, having no iron, which was treated with 2 *N* HCl and 0.8 *N* H_2SO_4 as before.

The optical density of the eluted iron was measured against this blank at the wave length of 305 mμ and found to be 0.012.

In this method, the amount of iron present in pyrolusite was calculated using the equation

$$C=\frac{O.D}{\epsilon}=\frac{\text{Optical density}}{\text{Extinction co-efficient}}$$

C = Concentration in molarity

$\epsilon = 2180$[7-8].

† Paper presented at the Convention of Chemists (1980) held at I. I. T., Bombay.

Manganese (KIO_4 method) : Portion of the electrophoregram containing manganese was treated with 2 N H_2SO_4 and manganese was extracted in the same way as iron. To this eluted solution, 5 ml 85% H_3PO_4, 20 mg $AgNO_3$ and 0.15 g potassium meta-periodate were added ; heated to boiling with stirring and kept at slightly below the boiling point for 1 hr. It was cooled and diluted to 50 ml in a volumetric flask.

The blank solution was prepared, as in the case of iron and similarly treated with H_2SO_4, H_3PO_4, $AgNO_3$ and KIO_4. The optical density of the eluted manganese solution was measured against this blank solution at 525 mμ and found to be 0.04.

A standard solution of manganous sulphate was prepared and a calibration curve for manganese was drawn from which the concentration of this eluted solution was calculated.

The percentages of iron and manganese in pyrolusite were calculated as given in Table 2.

TABLE 2

Constituents in pyrolusite as oxide	Optical densities of the eluted solutions after separation by paper electrophoresis	Concentration of the eluted solutions calculated from spectrophotometric method in terms of Fe and Mn in g/lit.	Percentage of Fe and Mn calculated from molar concentration, volume of migrants, volume of dilutents and weight of pyrolusite taken	Actual % of the constituents as Fe and Mn calculated by standard method
Fe	0.012	3×10^{-5}	6.17%	6.44%
Mn	0.04	11.60×10^{-5}	48.45%	53.26%

Standard methods for estimation of iron and manganese : Iron and manganese were estimated titrimetrically using standard dichromate as usual.

Alloy analysis :

Preparation of Indian coin solution The coin (2.4937 g) was taken in a conical flask and 10 ml conc. HNO_3 was added. It was then heated and allowed to react till all the alloy dissolved. The solution was diluted with water, 0.5 g urea added and heated nearly to boiling to decompose the nitrous fumes. The solution was transferred quantitatively into a 100 ml volumetric flask and the volume was made up to the mark with water.

Experimental procedure : Quantitative separation of the constituents of coin was possible electrophoretically using 0.1 M sodium formate as carrier electrolyte. The vertical apparatus was used for the paper electrophoretic separation of the main constituents of the coin solution. Potential gradient of 2.2 volts/cm for 3 hr run was maintained. After electrophoresis the electrophoregram was dried and developed carefully avoiding spreading of the zones. The electrophoregram was developed with yellow ammonium sulphide. A brown band for Cu(II) and a black one for Ni(II) were located and an attempt was made to estimate copper and nickel from the band spectrophotometrically.

The separation of the principal constituents (copper and nickel) is shown in Table 3, where '+' stands for anionic movement and '−' for cationic movement. The solution used for separation was 0.004 ml.

TABLE 3—CARRIER ELECTROLYTE 0.1 M SODIUM FORMATE

Migrant	Separation sequences of the migrant and the distance traversed by the zone in cm	
	Copper	Nickel
Coin	−0.8 to −1.9	−5.8 to −6.3

Estimation of copper ("Neo-cuproin" method) : After electrophoresis, the electrophoregram was dried and the portion of the strip containing copper was cut out from the electrophoregram after matching the said portion against the stained marked strip.

The region of the strip containing copper was treated with 2 N H_2SO_4 and copper was extracted as in the case of iron. Total volume was 15 ml. From the extracted solution 5 ml was taken. To the 5 ml solution in a separatory funnel, 5 ml of 10% hydroxyl-ammonium chloride solution to reduce Cu(II) to Cu(I) and 5 ml of a 30% sodium citrate solution to complex any other metals present, were added. Ammonia solution was then added for adjustment of the pH to about 4 (with congored paper), followed by 5 ml of 0.1% solution of "neocuproin" (2,9-methyl-1,10-phenanthroline) in absolute ethanol. It was shaken for about 30 sec with 5 ml of chlorofrom and the layers were allowed to separate. A further extraction with 2.5 ml of chloroform was carried out. The optical density at 457 mμ against a reagent blank was measured and found to be 0.575.

A standard solution of copper sulphate was prepared and a calibration curve for copper was drawn from which the extinction coefficient of copper was calculated.

Using this extinction co-efficient the concentration of copper in the eluted solution was calculated. The percentage of copper in coin (25 paise) was then calculated as given in Table 4.

TABLE 4

	Optical densities of the eluted solution after separation by paper electrophoresis	Concentration of the eluted solution calculated from spectrophotometric method in terms of Cu and Ni in g mole/lit	Percentage of Cu and Ni calculated from molar concentration, volume of migrant, volume of dilutents and weight of coin taken	Actual % of Cu and Ni calculated by standard method analysis
Cu	0.75	7.56×10^{-6}	72%	74.2%
Ni	0.009	0.95×10^{-6}	26.1%	26.3%

Estimation of nickel (dimethylglyoxime method) : The region of the strip containing nickel was treated with 2 N H_2SO_4 and nickel was extracted in

the usual procedure. The extracted volume of nickel solution was 10 ml. The solution was taken in a 50 ml volumetric flask. To 10 ml of the solution 5 ml of 10% citric acid solution was added and neutralised with ammonia, a few drops of which was added in excess ($pH > 7.5$). Then 3 ml of 1% dimethyl glyoxime in ethanol was added. The solution was extracted with three 3 ml portion of chloroform, shaking for 30 sec each time. The combined chloroform was shaken with 6 ml of 0.5 *M* ammonia (1 : 30). The ammonia washing was shaken with 2 ml of chloroform and the latter was added to the main chloroform extract. The nickel was returned to the ionic state by shaking the chloroform extract vigorously for 1 min with two 5 ml portions of 0.5 *M* HCl. The HCl solution was transferred to a 50 ml volumetric flask, diluted to about 50 ml, 1 ml of saturated Br_2 water added, followed by 2 ml of conc. ammonia. 1 ml of 1% dimethylglyoxime solution was added and diluted up to the mark. After 5 min the optical density at 445 mμ against a blank was measured and found to be 0.009.

A standard solution of nickel sulphate was prepared to obtain a calibration curve for nickel.

The extinction co-efficient of nickel was used to calculate its concentration in the eluted solution. The percentage of nickel in Indian coin (25 paise) was then calculated from the concentration term as shown in Table 4.

Using the equation,

$$O.D. = E.C. 1$$

the extinction co-efficient of copper and nickel were calculated. The extinction co-efficients (E) 0.76×10^4 for copper and 0.094×10^4 for nickel were obtained.

So, the amounts of copper and nickel present in the coin (25 paise) were calculated by the equation,

$$C = \frac{O.D.}{E} \text{ in molarity}$$

Standard method for estimation of copper and nickel: Copper was estimated gravimetrically using ammonium thiocyanate and nickel using dimethylglyoxime as usual.

It can be said from the experimental data that paper electrophoresis technique can equally be applied for analysis of pyrolusite and Indian coin.

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NOTES

Nickel(II) Complexes with Substituted Amino Benzothiazoles

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IN our recent work[1,2] we reported the synthesis of a series of Co(II), Cu(II) and Hg(II) complexes with substituted amino benzothiazoles. As an extension of the previous studies, the present communication describes the preparation and characterisation of some Ni(II) complexes with the monodentate ligands, 2-amino-6-methyl benzothiazole and 2-amino-6-chloro benzothiazole.

Experimental

All the chemicals used were of AnalaR grade. The substituted amino benzothiazoles have been synthesised by standard procedure[3].

Preparation of the complexes : Methanolic solution of the nickel(II) salts were reacted separately with methanolic solution of the substituted amino benzothiazoles in 1 . 2 ratio and refluxed for about 2 hr. Crystalline compounds separated out on cooling. These were filtered, washed with methanol followed by ether and dried *in vacuo*.

Metal contents of the complexes were estimated gravimetrically as dimethyl glyoximate. Nitrogen and sulphur were estimated by standard procedure. Conductance was measured in 10^{-3} *M* acetone solution using Toshniwal conductivity bridge. IR spectra were recorded in KBr phase using Unicam Sp-1025 spectrophotometer. Electronic spectra of the complexes in chloroform solution were recorded by using Hilger Watt Uvispeck spectrophotometer.

Results and Discussion

All the eight complexes reported in the present investigation are of the composition $[Ni(L_2 \text{ or } L'_2)X_2]$ and $[Ni(L_4 \text{ or } L'_4)]Y_2$, where $X=Cl^-$, NO_3^-, SCN^- and $Y=ClO_4^-$; L = 2-amino-6-methyl benzothiazole and L′ = 2-amino-6-chloro benzothiazole. All the complexes of the composition $[Ni(L_2 \text{ or } L'_2)X_2]$ are yellow to deep brown in colour whereas the two perchlorate complexes are green in colour. The complexes have low melting points and are soluble in acetone in which medium they are found to be non-electrolytes, the Λ_M being in the range of 10-25 mhos cm^2 except for the perchlorate complexes. The Λ_M values of the two perchlorate complexes are found to be around 230 mhos cm^2 indicating 1 : 2 electrolytic nature of these complexes.

The ir spectra show a sharp peak at $\sim$815 cm^{-1} in the free ligands which can be assigned[1] to ν(C–S) vibrations. On complexation, this frequency is shifted down to lower frequency region of $\sim$800 cm^{-1} indicating the bonding of the benzothiazole molecule to metal ions through ring sulphur atom. The bands observed[4] around 1535 and $\sim$3250 cm^{-1} in the free ligands are due to ν(C=N) and ν(N–H) vibrations, respectively. No change of these bands has been noticed in the complexes which conclusively proves that both the

TABLE 1—ANALYSIS, CONDUCTANCE, MAGNETIC SUSCEPTIBILITY AND IR SPECTRAL DATA

Compound	%Metal Found (Calcd.)	%N Found (Calcd.)	%S Found (Calcd.)	Λ_M mhos cm^2	μ_{eff} B.M.	ν(C–S)
$[NiL_2Cl_2]$	12.74 (12.83)	12.08 (12.23)	13.82 (13.98)	10.8	—	805
$[NiL'_2Cl_2]$	11.60 (11.77)	11.12 (11.23)	12.70 (12.83)	11.6	—	795
$[NiL_2(NO_3)_2]$	11.41 (11.49)	16.34 (16.44)	12.40 (12.58)	16.5	—	800
$[NiL'_2(NO_3)_2]$	10.52 (10.64)	15.10 (15.22)	11.42 (11.60)	18.0	—	800
$[NiL_2(SCN)_2]$	11.58 (11.67)	16.59 (16.71)	25.34 (25.46)	22.4	—	810
$[NiL'_2(SCN)_2]$	10.66 (10.80)	15.36 (15.45)	23.40 (23.54)	20.8	—	805
$[NiL_4](ClO_4)_2$	6.30 (6.42)	12.16 (12.26)	13.92 (14.01)	225.0	3.30	800
$[NiL'_4](ClO_4)_2$	5.72 (5.89)	11.12 (11.25)	12.72 (12.85)	228.0	3.60	795

L = 2-amino-6-methyl benzothiazole.
L′ = 2-amino-6-chloro benzothiazole.

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endo- and exo-cyclic nitrogen atoms are not bonded to the metal ions. In the nitrato complexes, absorption bands appear in the region ~1280 and 1400 cm^{-1}. The position of ν_4 and ν_1 and their separation ($\Delta\nu$) of ~120 cm^{-1} suggest[5-7] the nitrato group to be monodentate in the two complexes. The thiocyanato complexes have two sharp bands at ~2080 and 735 cm^{-1} attributable[8,9] to ν(C≡N) and ν(C–S) vibrations, respectively of N-bonded terminal thiocyanato group. In the present investigation, an increase of 30-40 cm^{-1} relative to the free thiocyanate ion is indicative of N-bonded terminal thiocyanate group on the basis of previous observations[10]. The appearance of a broad hump in the region 1040-1150 cm^{-1} indicates[11-13] the presence of ionic perchlorate group in the two perchlorate complexes and this is also corroborated by the molar conductance data of these complexes.

The chloro-, nitrato- and thiocyanato complexes are found to be diamagnetic. The perchlorate complexes have high magnetic moments (3.6 to 3.8 B. M.) indicating[14] a tetrahedral environment.

Visible electronic spectra of the chloro-, nitrato- and thiocyanato nickel(II) complexes show absorption bands at ~19800 and 20000 cm^{-1} and have relatively high extinction coefficient values, indicative of a square configuration. In case of the perchlorate complexes, two bands are observed at ~15200(180) and 8100(35) cm^{-1} attributable to $^3T_{1g}(F) \rightarrow {^3T_{1g}}(P)$ and $^3T_{1g}(F) \rightarrow {^3A_{2g}}$ transitions, respectively. The high molar absorptivity values of the former band and the high magnetic moment values suggest[16] a possible tetrahedral geometry for the two complexes.

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Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with Chelating Bidentate Schiff's Base

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We have been trying to synthesise complexes of rare coordination number through complexation of polydentate ligands with divalent metal salts. Earlier, we reported[1-4] metal complexes with bi-, tri- and tetradentate ligands having oxygen-nitrogen oxygen-sulphur, nitrogen-sulphur and oxygen-nitrogen-sulphur as the potential bonding sites. The present communication describes the synthesis and characterisation of six metal complexes with a new bidentate Schiff's base derived from benzoin and aniline.

Experimental

All the chemicals were analytical reagent grade products.

Preparation of the Schiff's base : To a methanolic solution of benzoin (2.12 g) and aniline (1.0 ml) was added anhydrous sodium acetate (4.0 g) and the mixture was refluxed for 1 hr over a water bath. The hot solution was poured into ice-cold water when a yellowish crystalline precipitate of the Schiff's base separated out. It was filtered, washed with water, dried and recrystallised from rectified spirit, m. p. 130°, yield 60%. (Found : C, 82.64 ; H, 5.52 ; H, 4.84. $C_{20}H_{16}ON$ requires C, 83.91 ; H, 5.59 ; N, 4 89 %)

Preparation of the complexes : Ethanolic solutions of the metallic chlorides were treated separately with ethanolic solution of the Schiff's base in 1 : 2 molar ratio followed by drop-wise addition of ammonia when metallic chelates separated out. These were filtered, washed with ethanol followed by ether and dried *in vacuo*.

Metal content of the complexes was estimated by complexometric EDTA titration method. The conductance measurements were carried out with a Toshniwal conductivity bridge in 1×10^{-3} *M* acetone solution of the complexes. Magnetic susceptibility measurements were made at room temperature using Gouy method. Electronic spectra were recorded in 1×10^{-3} *M* chloroform solution of the complexes using Hilger Watt Uvispeck spectrophotometer. The infrared spectra on Nujol mulls

TABLE 1—ANALYSIS, CONDUCTANCE, MAGNETIC SUSCEPTIBILITY AND IR SPECTRAL DATA

Compound	m.p. °C	Colour	% metal Found (Calcd.)	% N Found (Calcd.)	Λ_M mhos cm²	μ_{eff} B.M.	ν(C–O)	ν(C=N)
LH	180	Yellow	–	4.85 (4.89)	–	–	1210	1600
CoL_2B_2	142	Pink	8.81 (8.86)	4.17 (4.21)	14.5	4.85	1200	1590
NiL_2B_2	280	Light green	8.75 (8.82)	4.18 (4.22)	12.0	3.00	1200	1585
CuL_2	251	Blue	9.92 (10.08)	4.38 (4.41)	10 5	1.8	1205	1590
ZnL_2	224	White	10.15 (10.28)	4.35 (4.40)	15.0	–	1200	1590
CdL_2	122	White	16.38 (16.47)	3.95 (4.10)	12.5	-	1200	1590
HgL_2	126	Yellowish white	25.76 (26.08)	3.52 (3.63)	10.0	–	1205	1595

LH=Schiff's base derived from benzoin and aniline
B=H_2O.

were recorded using Unicam SP 200 spectrophotometer in the region 4000-650 cm^{-1}. Analytical, conductance, magnetic susceptibility and ir spectral data are recorded in Table 1.

Results and Discussion

Complexes reported in the present investigation have the composition [ML_2B_2] and [$M'L_2$] where M=Co(II), Ni(II); M'=Cu(II), Zn(II), Cd(II), Hg(II); LH=Schiff's base derived from benzoin and aniline and B=H_2O. All the six complexes have fairly low melting points and low conductance values (Table 1), indicating their non-electrolytic nature. Magnetic moment values show the presence of three, two and one unpaired electrons in case of Co(II), Ni(II) and Cu(II) complexes, respectively.

The ir spectra of the Schiff's base and the metal complexes are quite illustrative. It can function as a bidentate ligand with the hydroxy oxygen and the imino nitrogen atom as the principal bonding sites. The ν(C–O) vibration in the ligand appears at 1210 cm^{-1}. The decrease of this frequency by 10-15 cm^{-1} in the metal chelate shows the bonding of the hydroxylic oxygen atom to the metal ions. Coordination of the azomethine nitrogen atom to the metal ions is probably indicated by the shift of ν(C=N) frequency to the lower side[9]. In the ir spectra of the Schiff's base, a strong band due to ν(C=N) appears at 1600 cm^{-1} whereas in the complexes this band is observed at ~15·0 cm^{-1}. In case of Co(II) and Ni(II) complexes, a broad hump is observed at ~3450 cm^{-1} indicating the presence of coordinated water[10,11].

In the electronic spectra of Ni(II) complex, three bands appear at 8.5(7), 13.5(7.5) and 25.0(18) kK region, assignable to $^3A_{2g}\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ transitions, respectively. Cobalt(II) complex exhibits two absorption bands at 21(26) and 9.0(10) kK regions attributable to $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ and $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ transitions, respectively. Molar absorptivity values, position of absorption bands and magnetic moment values indicate high spin octahedral configuration for these complexes. One broad band is observed in case of Cu(II) complex at ~17.0(30) kK region. This broad band is a combination of $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2B_{2g}$ and $^2B_{1g}\rightarrow{}^2E_{1g}$ transitions corresponding to D_{4h} symmetry, indicating most probably a square planar configuration[12-14] for this complex.

From analysis, conductance and ir spectral studies, Zn(II), Cd(II) and Hg(II) complexes are found to be four coordinated having a tetrahedral environment around the metal ions.

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Binuclear Oxofluoro Complex of Quinquevalent Molybdenum

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VERY little work has been done on the oxofluoro complexes of Mo(V) compared to an extensive volume of work on the analogous oxochloro complexes. It is well known that paramagnetic oxochloromolybdates(V) hydrolyse as the acid concentration is decreased and ultimately dimerise to give oxo bridged diamagnetic or very weakly paramagnetic complexes. There are a few reports[1-3] till now on the preparation of oxo bridged Mo(V) fluoro complexes, but none of these has been adequately characterised. We have studied the magnetic susceptibility of $[MoOF_5]^{2-}$ at different HF concentrations and have isolated a binuclear complex $K_4[Mo_2O_4F_6].2H_2O$.

Experimental

$K_2[MoOF_5]$ and $MoO(OH)_3$ were prepared by methods reported earlier[1,4]. Molybdenum was analysed gravimetrically as oxinate[5], after decomposing the sample with fuming HNO_3 and H_2SO_4. The methods of analysis of potassium and fluorine and the determination of the oxidation state of molybdenum (by oxidation with dichromate) were described earlier[6,7].

Magnetic susceptibility was determined by Gouy method using $Hg[Co(NCS)_4]$ as calibrant. The diamagnetic corrections were taken from standard sources[8]. The magnetic susceptibility of K_2-$[MoOF_5]$ or $MoO(OH)_3$ in aqueous HF was measured at 30° using polythene tubes having ebonite stopper. The molybdenum content in aliquots was determined by oxinate method [after removal of F^- and oxidation of Mo(V)]. That all molybdenum was practically present as Mo(V) was checked by the determination of Mo(V) in aliquots by oxidation with dichromate.

Infrared spectra in the range of 4000-650 cm^{-1} were recorded using a Perkin Elmer spectrophotometer No. 257. Electronic spectra were recorded with Carl Zeiss DMR-21 and Carl Zeiss, Jena VSU2-P spectrophotometers.

Preparation of $K_4[Mo_2O_4F_6].2H_2O$: Potassium fluoride (14.0 g; 0.24 mole) dissolved in 2% HF was added to a concentrated solution of $MoO(OH)_3$ (1.0 g; 0.006 mole) in 2% HF. The brown red micro crystalline substance was separated by filtration and dried by pressing between filter papers and then keeping in a desiccator over H_2SO_4 and NaOH. The yield was 0.5 g (29%). (Anal. Found : Mo, 33.6 ; F, 20.0 ; K, 27.7. Calcd. for $K_4[Mo_2$-$O_4F_6].2H_2O$; Mo, 34.1 ; F, 20.3 ; K, 27.8%). The same compound was also obtained by mixing together aqueous solutions of $K_2[MoOF_5]$ (0.3 g) and KF (2.4 g).

Results and Discussion

The magnetic susceptibility of $K_2[MoOF_5]$ in HF medium has been measured as a function of the acid concentration. Because of the limited solubility of $K_2[MoOF_5]$ in dilute HF we preferred to use $MoO(OH)_3$. It is known[1] that $MoO(OH)_3$ dissolves in 40% HF from which green crystalline salts $M_2[MoOF_5]$ can be isolated by the addition of alkali metal fluorides. In a few representative cases it was checked that equimolecular solutions of $K_2[MoOF_5]$ and of $MoO(OH)_3$ in HF medium of identical concentration registered almost the same magnetic susceptibility.

The molar magnetic susceptibility of a solution of $MoO(OH)_3$ or $K_2[MoOF_5]$ in 40% HF was found to be about 1310×10^{-6} cgs units and the magnetic moment was 1.79 B.M. As the acid concentration was lowered the solutions turned from light green to brownish red and the susceptibility decreased. Ultimately, at an acid concentration of about 3%, the solution was diamagnetic. This behaviour of $[MoOF_5]^{2-}$ is very similar[9] to that of $[MoOCl_5]^{2-}$. The susceptibility of solutions of $MoO(OH)_3$ in dilute HF did not change on standing for half an hour.

$K_4[Mo_2O_4F_6].2H_2O$ is soluble in water from which it can be recrystallised. It loses the two molecules of water slowly at 140°. The molecular conductance of $1\times10^{-3}M$ aqueous solution (650 ohm^{-1} mol^{-1} cm^2) at 30° indicates some dissociation of the anion. The complex is very weakly paramagnetic (μ_{eff} is 0.20 B.M. at 30°). IR spectra give bands due to ν(OH) and $\delta(H_2O)$ at about 3500 and 1650 cm^{-1}. The terminal ν(Mo=O) modes appear at 950 vs, 925 vw and 905 m, while two bridging MoO_2Mo modes occur at 845 vs and 740 vs which agree with the presence of a bent MoO_2Mo bridge with the Mo=O groups on the same side of the bridge (i.e., *cis*)[10].

Like other complexes containing $Mo_2O_4^{2+}$ the electronic spectra of $K_4[Mo_2O_4F_6].2H_2O$ do not display the low energy transitions which are characteristics of monomeric MoO^{3+} complexes[10]. The reflectance or the Nujol mull spectra gave two bands at about 20,000 and 23,000 cm^{-1}.

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Polymeric Metal Complexes of 5,5'-(*p*-phenylene*bis*azo)-di-quinolin-8-ol

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THIS communication is in continuation of the previous work on metallated complexes of 5,5'-(benzidine*bis*azo)-8-hydroxyquinoline[1], and is a part of work on polymeric metal complexes being carried out in our laboratories[1-6]. The synthesis and characterization of the insoluble pigments derived from 5,5'-(*p*-phenylene*bis*azo)-di-quinolin-8-ol (abbr. PDQO) are now being reported

Experimental

The synthesis of 5,5'-(*p*-phenylene*bis*azo)-di-quinolin-8-ol was carried out by tetraazotizing 0.1 mol (10.8 g) of *p*-phenylenediamine and coupling the tetraazonium salt with 0.2 mol (29.0 g) of 8-quinolinol in pyridine medium as reported earlier[7].

Mixtures of 0.01 mol metal acetate hydrate [ammonium iron(II) sulphate in the case of Fe(II)] and 0.01 mol the above *bis*azo dye (4.20 g) were refluxed in DMSO for 6 hr to obtain the metallated complexes, which were filtered, washed with hot DMSO and dried as usual. The complexes were amorphous dark brown solids, insoluble in water and in the usual organic solvents.

The estimation of C, H, N and the metal, as well as spectral and thermal studies were done as described in an earlier communication[1].

Results and Discussion

The analytical data (Table 1) reveal a metal to ligand ratio of 1 : 1 as expected for a chain polymer, and the coordination of 2 H_2O per metal ion is inferred[8]. The ir spectra of the complexes of PDQO (Table 2) resemble closely those of the previously reported complexes of 5,5'-(benzidine*bis*azo)-8-hydroxyquinoline[1,8].

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TABLE 1—ANALYTICAL DATA OF POLYMERIC PIGMENTS OF PDQO

Empirical formula	Analysis%, Found (Calcd.)			
	C	H	N	M
$MnC_{24}H_{14}N_6O_2.2H_2O$	56.39 (56.58)	3.68 (3.53)	16.15 (16.50)	10.62 (10.82)
$FeC_{24}H_{14}N_6O_2.2H_2O$	56.27 (56.48)	3.69 (3.52)	16.42 (16.49)	10.71 (10.96)
$ZnC_{24}H_{14}N_6O_2.2H_2O$	55.19 (55.48)	3.56 (3.48)	16.11 (16.18)	12.40 (12.52)
$CdC_{24}H_{14}N_6O_2.2H_2O$	50.45 (50.88)	3.27 (3.18)	14.64 (14.84)	19.55 (19.88)

TABLE 2—ASSIGNMENT OF IR BANDS (cm^{-1})

PDQO	Mn(II)	Fe(II)	Zn(II)	Cd(II)	Assignment
—	3400-3350	3400-3350	3400-3350	3400-3350	$\nu OH(H_2O)$
3380-3120	—	—	—	—	νOH
—	1640	1640	1630	1630	$\delta OH(H_2O)$
1600	1590	1590	1595	1595	$\nu C=N$
1440	—	—	—	—	δOH
	1130	1130	1130	1130	$\nu C-O(C-O-M)$
	750	750	750	750	$\nu M-OH_2$
	625	625	625	625	$\nu M-O$
	460	460	460	460	$\nu M-N$

The electronic spectrum of the *bis*azo dye exhibits a band at 500 nm whose high intensity and wavelength suggest a $\pi \rightarrow \pi^*$ transition attributed to the extensive conjugation resulting in lowering of the π^* orbital energy[9]. The $d-d$ transition bands appear as weak shoulders on the intraligand band. The position and assignment of these bands are given in Table 3. Octahedral geometry around the central metal is assigned[10], which is in accordance with that previously reported for Co(II), Ni(II) and Cu(II) complexes[8]. In Fe(II) complex of lower symmetry, the E_g and T_{2g} states further split into A_{1g}, B_{1g} and B_{2g}, E_g.

TABLE 3—ELECTRONIC SPECTRA OF Mn(II) AND Fe(II) PIGMENTS

Metal	Band (nm)	Assignment	Geometry
Mn(II)	580	$^6A_{1g} \rightarrow {}^4T_{1g}$ (G)	Octahedral
	490	$\rightarrow {}^4T_{2g}$ (G)	
	440	$\rightarrow {}^4A_{1g}$ (G)	
	380	$\rightarrow {}^4E_g$ (G)	
	350	$\rightarrow {}^4T_{2g}$ (D)	
	330	$\rightarrow {}^4E_g$ (D)	
Fe(II)	720	$^5B_{2g} \rightarrow {}^5B_{1g}$	Octahedral

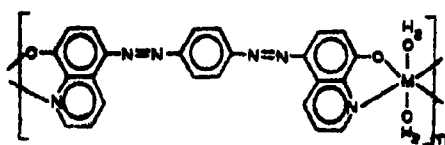
Doubling of band is anticipated. It is assumed that the ground state is B_{2g} for these complexes, then $^5B_{2g} \rightarrow {}^5B_{1g}$ is $10D_q$[8,7].

The modes of decomposition of these pigments resemble those of the previously reported complexes[1,8]. The chelates begin to lose weight at an accelerated rate between 300-380° (Table 4). The

TABLE 4—TGA DATA OF COMPLEXES

Temp. °C	% Weight loss of pigment containing			
	Mn(II)	Fe(II)	Zn(II)	Cd(II)
100	0.19	...	7.10	4.94
120	0.65	...	8.68	5.85
160	1.57	...	10.62	8.65
200	2.68	...	18.15	9.67
240	4.79	...	14.78	12.92
280	8.63	15.87	17.89	16.06
300	12.85	20.87	21.02	18.27
320	20.92	22.92	23.68	22.58
340	24.76	25.00	25.52	24.88
360	26.10	29.16	27.68	26.28
380	27.44	82.40	28.94	27.89
400	28.21	82.40	30.26	29.45
500	33.20	41.60	56.57	47.31
600	41.91	48.14	85.52	61.72
700	47.79	56.94	86.02	78.49
800	58.74	58.88	85.52	78.49
900	60.07			78.49

weight loss at temperatures lower than this range lies between 20-26%. The order of thermal stability is Cd(380°) $>$ Mn(320°) $>$ Fe(300°) $\sim$ Zn(300°). The weights of the residues do not conform to those of the metal oxides.

The insolubility of the pigments, composition, ir spectra and thermal stability are evidences of their polymeric structure, as given below.

M = Mn(II), Fe(II), Zn(II), Cd(III),
n = degree of polymerisation.

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Mixed Ligand Complexes of Zinc(II)

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DIVALENT zinc ion has completely filled $3d^{10}$ non-bonding shell and hence usually forms four coordinated tetrahedral compounds utilizing $4s4p^3$ hybrid orbitals for bonding. If experimental conditions are favourable, the coordination number can be increased to five involving one 4d orbitals[1-3]. This communication describes the mixed ligand complexes of the type $M[Zn(\beta\text{-dik})_2L]$ and $Zn(\beta\text{-dik})_2L'$ where M = K^+, Na^+ or Me_4N^+ ; β-dik = acetylacetonate or dibenzoylmethanate ; L = SCN^-, N_3^- or CN^- and L' = imidazole, morpholine and their derivatives.

Experimental

The β-diketonates of Zn(II) were prepared by the usual method[4]. Their thiocyanate, cyanide and azide adducts were obtained by refluxing the solutions of β-diketonates of Zn(II) in methanol with methanolic solutions of potassium thiocyanate, cyanide or sodium azide in 1 : 1 molar ratio for 2 to 3 hr. The mixed ligand complexes separated out on cooling. The compound $K[Zn(bzbz)_2(SCN)]$ so formed was treated with tetramethyl ammonium chloride in methanol. The precipitated potassium chloride was filtered off. The filtrate was evaporated to get the mixed ligand complex $Me_4N[Zn(bzbz)_2(SCN)]$. The complexes of the type $Zn(\beta\text{-dik})_2L'$ were prepared by refluxing Zn(II) acetylacetonate with imidazole, morpholine and their derivatives in methanol for 30 min to 2 hr. Morpholine and 2-methyl imidazole adducts separated out after keeping the solution overnight whereas other compounds separated out after 3 days. All the compounds were suction filtered, washed several times with ethanol to ensure complete removal of the excess ligand, followed by ether and dried *in vacuo*.

The composition of the complexes was established by estimating zinc as $ZnNH_4PO_4$, sulphur as $BaSO_4$ after oxidizing with bromine in carbontetrachloride solution and nitrogen by Kjeldahl method[5]. The conductance measurements were carried out with $\sim 10^{-3}$ *M* solutions in acetone, pyridine and methanol medium using Toshniwal conductivity bridge and a dip type cell. The infrared absorption spectra were recorded on Nujol mull using Unicam SP-200 double beam spectrophotometer. The physical, analytical, conductance and infrared spectral data are given in Tables 1 and 2, respectively.

Results and Discussion

For the compounds of the type $M[Zn(\beta\text{-dik})_2L]$, the molar conductance data indicate them to be

TABLE 1

Sl. No.	Compound	Colour	m.p. °C	Zn% Found (Calcd.)	S% Found (Calcd.)	N% Found (Calcd.)	Λ_M mhos (medium)
1.	$K[Zn(acac)_2(SCN)]$	White	>250	18.0 (18.1)	9.1 (8.8)	—	155 (acetone)
2.	$Na[Zn(acac)_2(N_3)]$	White	>250	20.0 (19.9)	—	—	66 (pyridine)
3.	$Me_4N[Zn(bzbz)_2(SCN)]$	Light orange	165	10.0 (10.1)	5.1 (4.9)	—	162 (acetone)
4.	$Na[Zn(bzbz)_2(N_3)]$	Yellowish white	>250	11.3 (11.8)	—	—	62 (pyridine)
5.	$K[Zn(acac)_2(CN)]$	White	>250	19.8 (19.9)	—	—	154 (acetone)
6.	$K[Zn(bzbz)_2(CN)]$	Light orange	>250	11.2 (11.3)	—	—	127 (methanol)
7.	$Zn(acac)_2(moph)$	White	223	18.3 (18.6)	—	4.0 (3.9)	18.2 (pyridine)
8.	$Zn(acac)_2(I.Z.)$	Pinkish white	135	19.6 (19.7)	—	4.0 (4.2)	24.5 (pyridine)
9.	$Zn(acac)_2(2Me.I.Z.)$	Light yellow	90	18.8 (18 9)	—	3.9 (4.0)	26.0 (pyridine)
10.	$Zn(acac)_2(B.I.Z)$	White	>250	16.4 (16 3)	—	3.2 (3 4)	27.3 (pyridine)
11.	$Zn(acac)_2(2Me B.I.Z)$	White	215	15 6 (15.5)	—	3.3 (3.3)	25.4 (pyridine)

TABLE 2—INFRARED SPECTRAL DATA IN cm^{-1}

Sl. No	Compounds	β-diketone		Thiocyanate or cyanide		Azide			
		$\nu(C-C)$	$\nu(C-O)$	$\nu(C-N)$	$\nu(C-S)$	ν_{Asym}	ν_{sym}	$\nu(N-H)$	$\nu(N-H)$
1.	$K[Zn(acac)_2(SCN)]$	1600s	1520s	2035vs	715s	—	—	—	—
2	$Na[Zn(acac)_2(N_3)]$	1605s	1525s	—	—	2080s	1260s	—	—
3	$Me_4N[Zn(bzbz)_2(SCN)]$	1605vs	1530vs	2060vs	710s	—	—	—	—
4	$Na[Zn(bzbz)_2(N_3)]$	1600s	1535s	—	—	2040s	1275s	—	—
5.	$K[Zn(acac)_2(CN)]$	1600s	1520s	2040m	—	—	—	—	—
6	$K[Zn(bzbz)_2(CN)]$	1605s	1525s	2055m	—	—	—	—	—
7.	$Zn(acac)_2(moph)$	1605vs	1550vs	—	—	—	—	1425m	3255m
8.	$Zn(acac)_2(I.Z.)$	1613s	1555s	—	—	—	—	1428m	3350m
9.	$Zn(acac)_2(2Me.I.Z.)$	1610vs	1530vs	-	—	—	—	1440sh	3270m
10.	$Zn(acac)_2(B.I.Z.)$	1605s	1525s	—	—	—	—	1430m	3300m
11.	$Zn(acac)_2(2Me.B.I.Z.)$	1596vs	1520vs	—	—	—	—	1418sh	3360m

s = sharp vs = very sharp m = medium sh = shoulder

1 : 1 electrolytes. The absorption due to $\nu(C-C)$ and $\nu(C-O)$ are shifted to lower frequencies due to metal ligand π-linkage superimposed on L→M σ bond[6]. $\nu(C-N)$ bands appear at 2030 and 2060 cm^{-1} and $\nu(C-S)$ appears at ~715 cm^{-1} indicating the presence of terminal S-bonded thiocyanate group[7]. The ionic KN_3 absorbs at 2042 cm^{-1} (ν_{asym}) and 1344 cm^{-1} (ν_{sym})[8]. In the compounds under report, the strong bands observed for ν_{sym} and ν_{asym} are in accordance with the earlier observations[9,10].

For complexes of the type $Zn(\beta\text{-dik})_2L'$, the molar conductance data indicate them to be non-electrolytic. The $\nu(M-O)$ of $Zn(acac)_2$ is shifted to lower frequencies upon adduct formation showing direct coordination of donor molecule with the metal ions. The absence of absorption band[8] at 3490 cm^{-1} due to coordinated water and the presence of absorption bands[11] at ~1430 and ~3300 cm^{-1} due to (N – H) bending and stretching frequencies clearly indicate the presence of N-donor ligands which have replaced the coordinated water from the parent compound. The compounds No. 3, 4, 6, 8, 9 exhibit light colours due to presence of the mixed ligands like other complexes[12,13] of Zn(II) and Cd(II). Hence all the complexes are presumed to be penta coordinated.

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Studies of ESR Spectra of Some Cu(II) Complexes

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THE esr spectra of copper(II) complexes have been studied by many workers[1-8]. Some of these studies have led to useful conclusion regarding the stereochemistry of Cu(II) in these complexes and the nature of metal-ligand bonding. Detailed esr studies on Cu(II) ion, bonded to oxygen, nitrogen and sulphur atom of the ligand, have been reported[9,10]. The authors have studied the metal-ligand bond strengths using esr data and the findings are presented here.

Materials and methods :

The copper(II) complexes studied in the present investigation are (i) $Cu(HMMCO)_2.3H_2O$ and $Cu(HBMMCO)_2.3H_2O$ (HMMCO = 2′-hydroxy-4-methoxy-5′-methylchalkone oxime, HBMMCO = 2′-hydroxy - 3′ - bromo-4-methoxy-5′-methylchalkone oxime) ; (ii) $Cu(TMBHA)_2.3H_2O$ (TMBHA = N-*m*-tolyl-*p*-methoxy benzohydroxamic acid) and $Cu(BPPTB)_2.2H_2O$ (BPPTB = 4-S-benzyl-1-*p*-Cl-phenyl-5-phenyl-2,4-isodithiobiuret). These complexes were prepared by the methods described earlier[11-14]. Electronic spectra, magnetic measurement, conductivity etc. suggest tetragonal symmetry to these complexes[11-14].

The esr spectra of copper(II) complexes of HMMCO and BPPTB were taken at room temperature and liquid nitrogen temperature in chloroform solution (Fig. 1). ESR spectra of copper(II) complexes of HMMCO, HBMMCO, TMBHA and BPPTB were taken in polycrystalline state at room temperature only (Fig. 2).

The esr spectra of the same copper complexes at room temperature and liquid nitrogen tempearature were obtained from the Regional Sophisticated Instrumentation Centre, I.I.T., Madras. The esr spectra of some copper complexes at room temperature were also run for us by the E.S.R. Laboratory, I.I.T., Bombay

Results and Discussion

The esr spectra were analysed by the method of Kneubuhl[15], Sands[16] and Garman *et al*[14]. The g values at room temperature are presented in Table 1 and the hyperfine coupling constants and g values at liquid nitrogen temperature are shown in Table 2. The nature of esr spectrum (Fig. 1 and Fig. 2) of copper(II) complexes in the present study
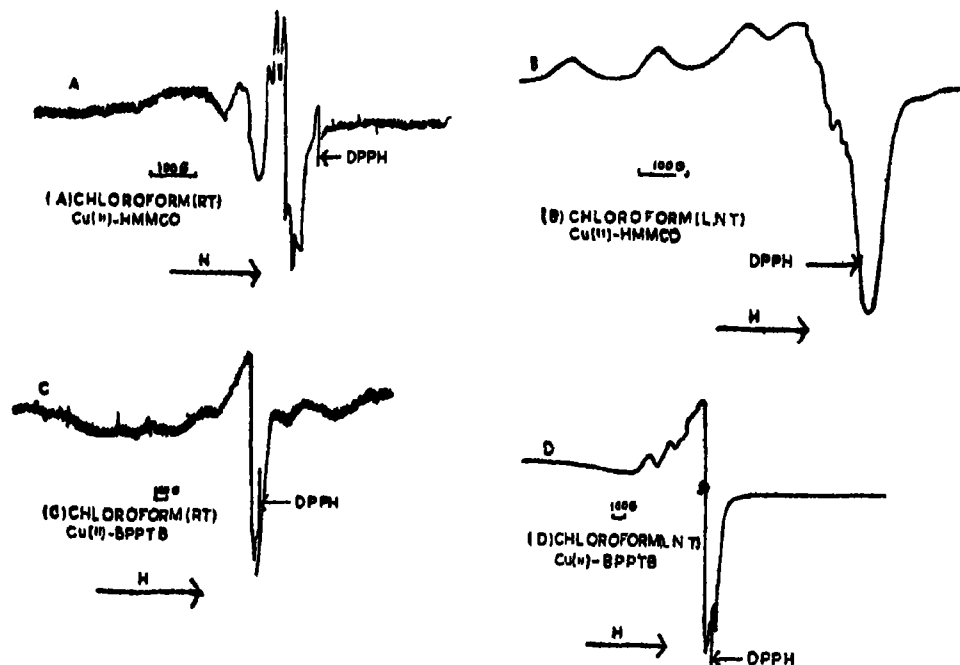
Fig. 1
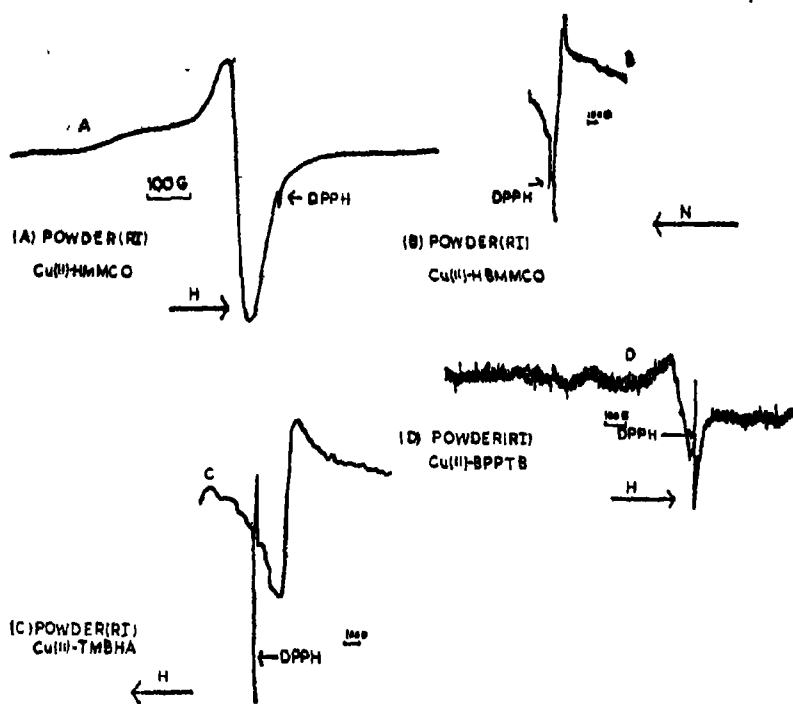
Fig. 2

is indicating a tetragonal symmetry[27-30]. This fact supports the observations made on the basis of magnetic and spectral studies[21-24].

TABLE 1—ESR SPECTRA OF POLYCRYSTALLINE COPPER(II) COMPLEXES AT ROOM TEMPERATURE

Copper(II) complexes of	$g_{\parallel}$	$g_{\perp}$	$\lvert g \rvert$
HMMCO	2.217	2.049	2.105
HBMMCO	2.241	2.088	2.105
TMBHA	2.255	2.040	2.111
BPPTB	2.214	2.028	2.090

$\lvert g \rvert = \frac{1}{3}(2g_{\perp}+g_{\parallel})$

TABLE 2—ESR SPECTRA OF COPPER(II) COMPLEXES AT ROOM TEMPERATURE AND LIQUID NITROGEN TEMPERATURE IN CHLOROFORM

Copper(II) complexes of	$g_{\parallel}$	$g_{\perp}$	$\lvert g \rvert$	$A_{\parallel}$ $10^{-4}\times cm^{-1}$	$A_{\perp}$	$\lvert A \rvert$
HMMCO	2.200	2.041	2.094	163.95	18.73	67.13
BPPTB	2.204	2.035	2.091	168.64	32.79	78.07

$\lvert A \rvert = \frac{1}{3}(2A_{\perp}+A_{\parallel})$

Kivelson and Neiman[8] showed that $g_{\parallel}$ is a moderately sensitive function for indicating covalency; for ionic environment $g_{\parallel}$ is normally > 2.3, for covalent environment it is < 2.3. In view of this, covalency of the M – L band in the present Cu(II) complexes follows the order BPPTB > HMMCO > HBMMCO > TMBHA.

g_{av} value of HMMCO and BPPTB in polycrystalline state is nearly the same as that of the value obtained in chloroform solution. Therefore, it is quite probable that the arrangement of copper(II) ion in polycrystalline state and in chloroform solution may be the same[10]. Super haperfine lines are clearly observed in the esr spectra of HMMCO (in frozen state) in the region between parallel and perpendicular components. This may perhaps come from the nitrogen atom as is observed in some other cases[1]. The nature of the σ and π bonds is investigated in the case of Cu(II)-HMMCO and Cu(II)-BPPTB systems where complete data are available (i.e. absorption peaks, $\lvert g \rvert$, $\lvert A \rvert$, $g_{\perp}$ and $A_{\perp}$ values). For electronic transitions Table 3 is referred.

TABLE 3—ASSIGNMENT OF THE ELECTRONIC TRANSITION IN CHLOROFORM SOLUTION

Copper(II) complexes of	$E_{xy}\leftarrow E_{x^2-y^2}$ $(B_{1g}\rightarrow B_{2g})kK$	$E_{yz,xz}\leftarrow E_{x^2-y^2}$ $(B_{1g}\rightarrow E_g)kK$
HMMCO	15.38	17.86
BPPTB	15.62	18.18

Molecular orbital theory put forward by Maki and McGarvey[4] is used to calculate metal-ligand bond nature. In fact, this theory is strictly applicable to square planar complexes. But many workers[20-22] applied this theory to complexes having other than square planar structure.

The approximate value of the plane bonding parameter α^2 can be estimated from the following simple expression:

$$\alpha^2 = \frac{\lvert A \rvert}{pK} + \frac{\lvert g \rvert - 2.0023}{K} \quad \ldots (1)$$

where, | A | and | g | are average A and g values, p is the free ion dipole term which is given a value of 0.036 cm^{-1} and K is the Fermi contact term which is actually given a value of 0.43.

To obtain in-plane and out-of-plane bonding parameters β^2 and γ^2 respectively, the following simplified expressions were used assuming tetragonal D_4h symmetry for Cu(II) in HMMCO and BPPTB complexes[18].

$$g_{\parallel} = 2.0023 - \frac{8\xi\alpha^2\beta^2}{\Delta E(B_{1g} \rightarrow B_{2g})} \quad \text{... (II)}$$

$$g_{\perp} = 2.0023 - \frac{2\xi\alpha^2\beta^2}{\Delta E(B_{1g} \rightarrow E_g)} \quad \text{.. (III)}$$

The symbol ξ represents the one electron spin orbit coupling coefficient ($= -828$ cm^{-1}).

The values of α^2, β^2 and γ^2 are set out in Table 4. The bonding parameter α^2 is a measure

TABLE 4—BONDING PARAMETERS OF COPPER(II) COMPLEXES

Copper(II) complexes of	α^2	β^2	γ^2
HMMCO	0.68	0.70	0.63
BPPTB	0.71	0.66	0.51

of the covalency of the plane σ bonding. A value of $\alpha^2 = 1$ indicates complete ionic character while $\alpha^2 = 0.5$ indicates essentially 100% covalent bonding. The β^2 and γ^2 parameters are a measure for covalency in the in-plane and out-of-plane bonding, respectively. β^2 or $\gamma^2 = 1$ indicates no covalent bond and β^2 and $\gamma^2 \approx 0.5$ corresponds to total covalent character.

The observed value of α^2, β^2 and γ^2 parameters in the present case are indicative of strong in-plane σ and π covalent bonding and out-of-plane π bonding. Out-of-plane covalency character is observed to be more in the BPPTB than in HMMCO complex which may be attributed to the presence of vacant d orbitals in sulphur atom of BPPTB. This favours back π bonding from metal to ligand.

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Stability Constants and Thermodynamic Parameters of Neodymium(III) Complexes with Mandelic, Cinnamic and Phenylacetic Acids: A Polarographic Study

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MANDELIC, cinnamic and phenylacetic acids were used as complexing agents for metals by different authors[1-4]. A survey of literature shows that the complexation study of rare earth metal ions with these ligands have not been reported polarographically. In the present paper the authors report the stability constants and thermodynamic parameters of neodymium(III) complexes with mandelic, cinnamic and phenylacetic acid.

TABLE 1—METAL LIGAND STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF THE COMPLEXES AT μ=1.0 M POTASSIUM CHLORIDE

		Mandelic acid 1 : 2		Cinnamic acid 1 : 1		Phenylacetic acid 1 : 1	
		25°	35°	25°	35°	25°	35°
Metal ligand stability constant log K	Neodymium(III)	6.5	6.0	3.2	2.7	4.3	3.8
Change in enthalpy (ΔH) in K cal/mole	Neodymium(III)	−20.5		−17.7		−24.0	
Change in free energy (ΔG) in K cal/mole	Neodymium(III)	−8.9	−8.5	−4.3	−3.9	−5.9	−5.3
Change in entropy (ΔS) in cal/degree/mole	Neodymium(III)	−39.0	−40.0	−45.0	−45.0	−60.9	−66.6

Experimental

A.R. grade chemicals were used to prepare all the solutions. The metal solution was prepared by dissolving the calculated amount of metal oxide in minimum hydrochloric acid and was standardized with EDTA[4]. The solutions of ligands were prepared in double distilled water.

The concentration of metal ion, gelatine and potassium chloride in the test electrolytic solution was fixed at 2 m*M*, 0.01% and 1.0 *M*, respectively. The ligand concentration was varied from 1.0 m*M* to 10.0 m*M*. Ionic strengtn was fixed at μ= 1.0 with potassium chloride. An Elico digital *p*H meter (Model L 1-120) was used to fix the *p*H of the test electrolytic solution at 2.4 ± 0.02.

An automatic pen recording (C.I.C., Baroda, India) polarograph was used to record the polarograms. The capillary used had an 'm' value of 2.20 mg/sec and drop time of 3.1 sec/drop when measured in an air free 1.0 *M* potassium chloride at 46.0 cm effective height of the mercury column. Pure nitrogen was used for deoxygenating the solution before recording the polarograms. All the measurements were carried out at 25° and 35°, thermostatically controlled.

Results and Discussion

Nd(III) gives a well defined reversible three-electron reduction wave in 1.0 *M* potassium chloride + 0.01% gelatin at *p*H 2.75[5-6]. The reduction of Nd(III) and Nd(III)-complexes with all the three ligands were found to be of diffusion controlled nature as the plots of i vs $\sqrt{h}$ yield straight lines passing through the origin. An analysis of the plots of $E_{d.e.}$ vs log $\frac{i}{i_d - i}$ and $E_{3/4} - E_{1/4}$ values for simple Nd(III) and its complexes with all the three ligands revealed the reversible nature of the reduction waves. The half wave potential of Nd(III) shifted to a more negative value on increasing the concentration of ligands. Lingane[7] method was used to find out the composition and stability constants of Nd(III) complexes with mandelic, cinnamic and phenylacetic acids. The thermodynamic parameters were calculated by the well known thermodynamic relations[8]. The composition, stability constants and thermodynamic parameters are given in Table 1.

The stability constants of 1 : 1 complexes with respect to the ligands was found to be greater for phenylacetic acid than for cinnamic acid which is the order of their basicity. The unsaturated double bond present in cinnamic acid also contribute to lower stability[3] to its metal complexes. Mandelic acid forms a chelate with the stoichiometry 1 : 2 giving maximum stability to its metal complex.

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Studies on the Flow and Sedimentation Characteristics of Sodium Bentonite Suspensions in Presence of Electrolytes and Humic Acids

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THE flow behaviour of a clay suspension is a very sensitive criterion for particle interaction. The changes in flow behaviour of clay suspensions upon (i) addition of different electrolytes, (ii) addition of the same electrolyte at different concentrations[1,2], (iii) addition of a polyelectrolyte, such as humic acids in (i) and (ii) above and (iv) changes of temperature in all the above cases[3], provide a means for analysis of changes in particle interaction forces and modes of particle association occurring in flocculation processes.

Guha and Gupta[4] have shown that the departure from linearity in the plot of volume concentration against relative viscosity can be taken to be the onset of structure formation. A viscometric study of the concentration dependence of dilute montmorillonite dispersions was made by Granquist[5] both in distilled water and electrolyte containing water. The flocculating effect of anionic polyelectrolytes suspended in water, in relation to the mechanism of formation of polyanion linkage among the clay particles was studied by Diazakita and Kawaguchi[6]. The present work comprises studies on (a) the effect of the addition of different amounts of NaCl to Na-bentonite suspensions of different concentrations at room temperature (30°), (b) the stabilizing effect of humic acids addition (in different concentrations) to each of the systems mentioned above and (c) the swelling properties of clay upon the addition of humic acids.

Experimental

Preparation of clay sample and its conversion to monoionic form and measurement of C. E. C. was done according to the method reported earlier[4]. The clay samples were characterised by chemical analysis (Table 1), B. E. T. surface area and C. E. C. measurements (Table 2).

The homogenised and non-settling clay suspension at a concentration where thixotropy was absent (0.8 % w/v) was mixed with different amounts of NaCl (the suspension made 0, 0.31, 0.62, 1.25, 2.5 and 5 N with respect to NaCl) and with different amounts of humic acids (1.1, 2.1, 3.5 and 4.6 mg of dry humic acids per 100 g of clay), equilibrated overnight and viscosities measured by a thermostated Ostwald viscometer at 30°. The plots of

TABLE—1

Chemical constituent	%
Loss on ignition	12.5
SiO_2	52.1
Al_2O_3	25.8
Fe_2O_3	4.7
MgO	2.1
K_2O	0.56
Na_2O	0.41

TABLE 2—THE C.E.C. AND B.E.T. SURFACE AREA OF THE SIZE SEPARATED SAMPLE

C.E.C. meq/100 g	180
Surface area m^2/g	158.5

relative viscosity versus volume concentration (of clay) at different electrolyte and humic acids concentrations are shown in Fig. 1 and Fig. 2.
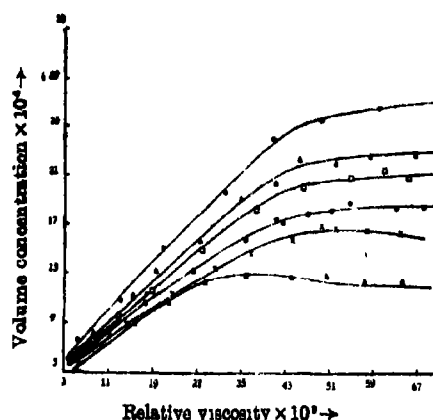
Fig. 1. Changes in the flow properties of Na-bentonite on the addition of NaCl of different concentrations.

○···No NaCl added　△···0.31 N NaCl added
□···0.62 N NaCl added　●·· 1.25 N NaCl added
×···2.5 N NaCl added　⊥··· 5 N NaCl added
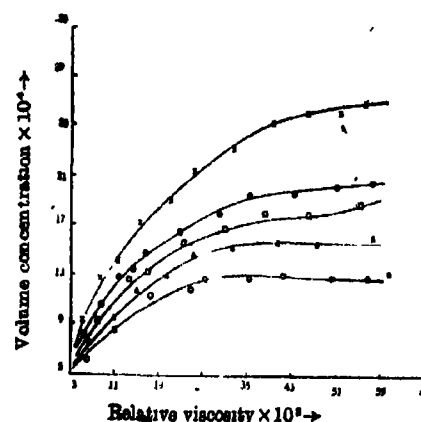
Fig. 2. Changes in the flow properties of Na-bentonite suspensions which is 5-N with respect to NaCl, on the addition of different amounts of humic acids.

○ ··· No humic acid added
△·· 1.1 mg/100 g of clay, humic acid added
□·· 2.1 mg/100 g of clay, humic acid added
⊙···3.5 mg/100 g of clay, humic acid added
×··4.6 mg/150 g of clay, humic acid added

a—Dept. of Physics and Mathematics; b—Dept. of Petroleum Engineering; c—Dept. of Chemistry, Fuel and Mineral Engineering.
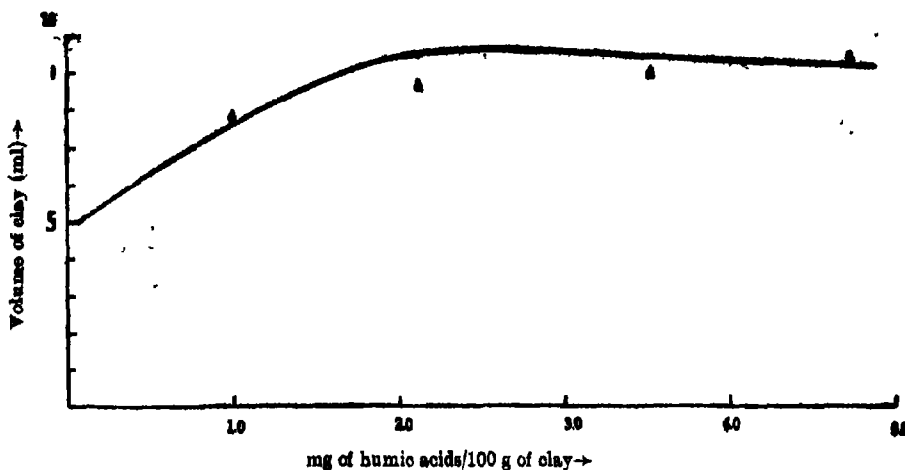
Fig. 3. Swelling of 0.8 Na-bentonite suspension flocculated by the addition of NaCl upon the addition of different amounts of humic acid.

For sedimentation volume studies, a 0.8% (w/v) sodium bentonite suspension was taken in a measuring cylinder and just enough 5 *N* NaCl solution was added until a clear supernatant liquid was observed. The suspension was left overnight and the volume of the suspension adjusted to 5 ml. Different amounts (1.1, 2.1, 3.5 and 4.8 mg) of humic acids were then added, the mixture homogenised for 4 hr and left overnight again. The final volume was then plotted against the amount of added humic acids (Fig. 3)

The humic acids used in this study were prepared by boiling powdered south Arcot lignite with 5 *N* NaOH, filtering and precipitating the humic acids with 2 *N* HCl. The precipitated humic acids were washed, dried in an air oven at 110° for 2 hr and cooled in a desiccator.

Discussion

Clay particles carry a negative charge, which is balanced by the cations adsorbed on their surfaces. Positive edge charges for montmorillonites have been reported by Van Olphen[10] and Meldau *et al*[8] but the magnitude of these edge charges is far too small compared to the surface negative charge on the clay plates. Schofield and Samson[9] reported that the flocculation of Na-kaolinite occurs due to the electrostatic attraction between positive edges and negative faces. No conclusive evidence of a similar mechanism exists for the flocculation of montmorillonite particles. The nature and extent of charge distribution in the clay particles is dependent on isomorphous lattice substitution of altervalent ions (e.g., Al^{3+} by Mg^{2+}) as well as lattice distortion. The positive adsorption sites are, however, dependent on the particle size distribution of the clay material.

The addition of an electrolyte compresses the electrical double layer, presumably at the negative surface[10] resulting in a stronger interparticle association with consequent change in viscosity. A departure from the linear Einstein relation would then be expected at a lower volume concentration with increasing electrolyte concentration.

The decreasing slope in the relative viscosity versus volume concentration (of clay) curves upon increasing electrolyte concentration (Fig. 1) supports this mechanism

A polyelectrolyte (such as humic acids) has a polar group attached to a non-polar macro-molecular tail. This will effectively screen the double layer from compression on the addition of an electrolyte. Thus, the addition of a polyelectrolyte is expected to annul or suppress the effect of electrolyte addition An increase in floc volume on the addition of a polyelectrolyte is also expected.

The increasing slope in the relative viscosity vs volume concentration (of clay) (Fig. 2) and increasing sedimentation volume (upto a limiting value) (Fig. 3) upon the addition of increasing amounts of humic acids supports this contention.

Conclusion : From a study of the flow properties of Na-bentonite suspensions in the presence of NaCl solutions of different concentrations and upon the addition of different amounts of humic acids, it was found that (a) electrolyte addition favours flocculation and reduction in viscosity of the suspensions and (b) humic acids (which are essentially polyelectrolytes) annul or suppress the effect of electrolyte addition and tend to increase the viscosity and floc volume of the clay suspensions.

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2-Aryl amino-4-[4'-(benzene sulphonamido)-phenyl]-thiazoles

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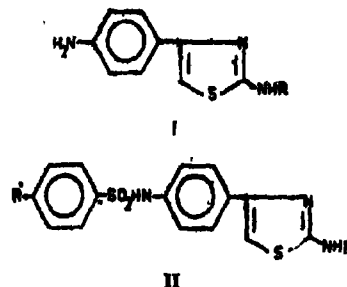
VARIOUS 2-substituted amino-4-[4'(benzene sulphonamido)-phenyl]-thiazoles have been synthesized to study their anti bacterial activity.

The starting materials, 4-(4'-aminophenyl)-2-aryl amino)-thiazoles, were synthesized by condensing *p*-acetamido-ω-chloroacetophenone with substituted phenyl thioureas in alcohol. The thioureas used were phenyl, *o*-, *m*- and *p*-chlorophenyl, *o*-methoxyphenyl, *o*-, *m*- and *p*-methylphenyl, *o*-nitrophenyl and (2"-pyridyl)-thioureas. 4-(4'-Acetamidophenyl)-2-(substituted amino)-thiazoles were hydrolysed to 4-(4'-aminophenyl)-2-(substituted amino)-thiazoles (I) which on reacting with *p*-substituted phenyl sulphonyl chloride yielded compounds of the type (II). It should be noted here that 4-(4'-acetamido-phenyl)-2-(substituted amino)-thiazoles did not give any reaction product with *p*-substituted phenyl sulphonyl chloride.

I

II

Hence, the primary amino group condenses with sulphonyl chloride group in the formation of the compounds (II). The ir spectra confirmed the presence of O=S=O grouping in these compounds from their strong absorption at ~1350 cm^{-1} (asymmetric stretch) and ~1125 cm^{-1} (symmetric stretch). The thiazole nucleus showed absorption bands at 1570–1530, 1438–1380 and 1390–1330 cm^{-1}. The two bands in the region 3500–3260 and 3220–3180 cm^{-1} are due to $-SO_2-NH$ and $-NH-$ stretchings. The $-NH-$ bending absorption was observed at 1610–1580 cm^{-1}.

Experimental

Melting points are uncorrected. The ir spectra were recorded on Perkin-Elmer-137 spectrophotometer in KBr phase.

Synthesis of 4-(4'-aminophenyl)-2-(substituted amino)-thiazoles (I): A mixture of *p*-acetamido-ω-chloro-acetophenone (0.1 mole), substituted phenyl

TABLE—1

Substituents R	4-(4'-aminophenyl-2(substituted amino)-thiazole (I)			4-[4'-(*p*-substituted benzene sulphonamido)-phenyl]-2(substituted amino)-thiazoles (II) — Substituent R': $-CH_3$			$-NHCOCH_3$			NH_2		
	m.p. °C	N% Found (Calcd.)	S% Found (Calcd.)	m.p. °C	N% Found (Calcd.)	S% Found (Calcd.)	m.p. °C	N% Found (Calcd.)	S% Found (Calcd.)	m.p. °C	N% Found (Calcd.)	S% Found (Calcd.)
Phenyl	121	15.52 (15.72)	11.54 (11.98)	143	10.12 (9.97)	15.30 (15.20)	152	11.97 (12.07)	14.48 (14.16)	162	13.14 (13.24)	15.60 (15.16)
o-Chlorophenyl	210	13.84 (13.95)	10.52 (10.68)	196	9.14 (9.23)	14.32 (14.06)	192	11.34 (11.23)	12.62 (12.85)	196	12.32 (12.24)	13.92 (14.03)
m-Chlorophenyl	104	13.81 (13.95)	10.61 (10.68)	179	9.40 (9.23)	14.40 (14.06)	124	11.27 (11.23)	12.59 (12.85)	191	12.28 (12.24)	14.37 (14.03)
p-Chlorophenyl	212	13.75 (13.95)	10.65 (10.68)	192	9.37 (9.23)	14.29 (14.06)	183	11.37 (11.23)	12.59 (12.85)	189	12.31 (12.24)	14.29 (14.03)
o-Methoxyphenyl	203	14.25 (14.14)	10.53 (10.77)	187	9.50 (9.27)	14.00 (14.19)						
o-Methylphenyl	142	14.65 (14.95)	10.32 (11.39)	188	9.71 (9.65)	14.92 (14.71)	192	11.74 (11.68)	13.22 (13.38)	180	12.93 (12.81)	14.62 (14.67)
p-Methylphenyl	157	15.01 (14.95)	11.49 (11.39)	217	9.73 (9.65)	14.95 (14.71)	146	11.57 (11.68)	13.29 (13.38)	226	12.87 (12.81)	14.06 (14.67)
o-Nitrophenyl	146	17.93 (18.12)	10.32 (10.25)	140	11.85 (12.02)	14.71 (13.73)	145	13.81 (13.75)	12.35 (12.75)	298	15.10 (14.95)	13.62 (13.73)
(2"-Pyridyl)-	240	20.74 (20.89)	11.72 (11.94)				179	14.94 (15.09)	14.98 (15.18)	184	16.64 (16.55)	15.29 (15.18)

thiourea (0.1 mole) and ethanol (55 ml) was refluxed for 1.5 hr. 4-(4'-Acetamido-phenyl)-2-(substituted amino)-thiazoles were isolated following the method of Hantzsh[1]. These compounds were refluxed with 2 *N* NaOH (14 ml) and ethanol for 45 min. Ethanol was distilled off and the reaction mixture poured in water. The solid product was filtered, washed and crystallised from ethanol. The melting points and analysis are given in Table 1.

General procedure for the synthesis of 4-[4'-(p-substituted benzene sulphonamido)-phenyl]-2-(substituted amino)-thiazoles (II) : A mixture of 4-(4'-aminophenyl)-2-(substituted amino)-thiazole (0.01 mole), *p*-substituted benzene sulphonyl chloride (0.01 mole) and dry pyridine (20 ml) was heated on water bath for 1.0 hr and then kept at room temp for 36 hr. The reaction mixture was poured in ice containing little conc H_2SO_4 with constant stirring. The crude product washed with dil $NaHCO_3$ soln and distilled water, was crystallised from ethanol.

p-Methyl- and *p*-acetamido benzene sulphonyl chloride were condensed with different 4-(4'-aminophenyl)-2-(substituted amino)-thiazoles. The 4-(4'-N-acetamido sulphonamido)-2-(substituted amino)-thiazole derivatives were hydrolysed with 2 *N* NaOH to 4-(4'-sulphanilamido)-2-(substituted amino)-thiazoles and crystallised from ethanol The melting points and analysis are given in Table 1.

Activity : Some representative compounds from each series were tested against four different organism viz , *V. comma*, *M. tuberculosis*, *S. typhi* and *S. aureus*. None of them was found to be active.

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Selective Methylation of Quercetin and Myricetin

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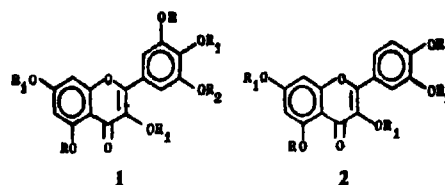
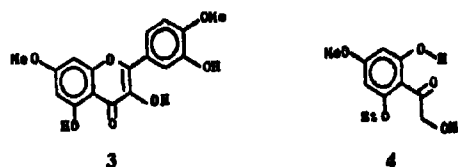
SEVERAL methods are known for selective methylation of flavonoids[1-3]. The key factor permitting methylation of certain hydroxyl groups in preference to others is the differential acidity of the hydroxyl groups placed at different positions of the flavone nucleus. The pioneering work in this direction was done by Simpson and Beton[1] who studied the methylation of flavones and flavonols with dimethyl sulphate in refluxing acetone in presence of sodium bicarbonate and postulated the acidity order of the flavone hydroxyls as 7>4'>3'>3 on the basis of the results. But recent spectroscopic data, particularly the observation[4] that flavones bearing a hydroxyl group at 3 rather than 3' position exhibit bathochromic shift in uv spectra in presence of a weak base like sodium acetate, clearly indicate the enhanced acidity of the hydroxyl group at 3 position compared to that at 3' position. This is clearly reflected in our selective methylation experiments with polyhydroxyflavones like myricetin (**1**, $R=R_1=R_2=H$) and quercetin (**2**, $R=R_1=R_2=H$) which gave in our hands 3,7,4'-trimethylethers (**1** and **2**, $R=R_2=H$, $R_1=Me$) as major products and 3,7,3',4'-tetramethyl ethers (**1** and **2**, $R=H$, $R_1=R_2=Me$) as the minor constituents. It was further observed that replacement of sodium bicarbonate with anhydrous sodium acetate gave essentially 7,4'-dimethyl ethers and the major product of methylation of quercetin with dimethyl sulphate in presence of sodium acetate was 7,4'-dimethylquercetin (**3**). The partially methylated flavonols were fully characterised from detailed spectral analysis of the compounds, their derivatives and also by degradative studies in some cases. Thus, the major compound obtained from myricetin yielded a triethylether (**1**, $R_1=Me, R=R_2=Et$)

which on alkali hydrolysis afforded ω,4-dimethoxy-2-ethoxy-6-hydroxy-acetophenone (**4**) and 3,5-diethyl-4-methyl gallic acid. Similarly, ethylation and subsequent alkali hydrolysis of the major product obtained from quercetin furnished the acetophenone, **4** and O-ethyl-isovanillic acid.

Experimental

Melting points were taken on a Toshniwal apparatus and are uncorrected. UV spectra were recorded on a Cary-14 instrument using spectrograde methanol (E.M.). IR spectra were recorded on a Perkin-Elmer 720 spectrophotometer in Nujol mull. ^1H NMR spectra were taken on Bruker WH-90 and Varian A-60D instruments using deuteriochloroform as solvent and TMS as internal standard. Anhydrous Na_2SO_4 was normally used

for drying organic solvents. Analytical samples were routinely dried over P_2O_5 for 24 hr *in vacuo*. Silica gel for column chromatography refers to B.D.H. (60-120 mesh).

Methylation of myricetin to 3,7,4'-trimethylmyricetin (1, R=R₂=H, R₁=Me) and 3,7,3',4'-tetramethylmyricetin (1, R=H, R₁=R₂=Me) : A mixture of myricetin (4 g), freshly distilled Me_2SO_4 (5 ml) and $NaHCO_3$ (25 g) was refluxed under anhydrous condition with dry Me_2CO (500 ml) for 12 hr. The reaction mixture was cooled, filtered and the filtrate was concentrated and chromatographed over a bed of silica gel (100 g). The column after initial washing with C_6H_6 to remove unreacted Me_2SO_4 was first eluted with $C_6H_6-Me_2CO$ (49 : 1) mixture to afford 3,7,3',4'-tetramethylmyricetin (0.8 g) and then with $C_6H_6-Me_2CO$ (19 : 1) to furnish 3,7,4'-trimethylmyricetin (2.5 g).

3,7,4'-Trimethylmyricetin crystallised from MeOH as fine yellow needles, m.p. 207-08° (Lit.[8] m.p. 208-10°), $C_{18}H_{16}O_8$, λ_{max} (MeOH) 262, 346 nm (log ε, 4.41, 4.36). MS : m/e 360(M^+), 346, 345, 332, 331, 317, 167. Found : C, 59.78 ; H, 4.64. $C_{18}H_{16}O_8$ requires C, 60.00 ; H, 4.48%. Colourless crystals of triacetate, $C_{24}H_{22}O_{11}$, m.p. 196-97° ; ^1H nmr : δ 2.35 and 2.45 (6H and 3H *s* each, 3-OAc), 3.84 and 3.89 (6H and 3H *s* each, 3 - OMe), 6.60 and 6.80 (1H *d* each, J=2.5 Hz, C-6 and C-8 H), 7.72 (2H, *s*, C-2' and C-6'-H). Found : C, 59.98 ; H, 4.72. $C_{24}H_{22}O_{11}$ requires C, 59.26 ; H, 4.56%. Triethylether $C_{24}H_{28}O_8$, m.p. 139°. Found : C, 64.34 ; H, 6.18. $C_{24}H_{28}O_8$ requires C, 64.85 ; H, 6.35%.

Alkali hydrolysis of 3,7,4' trimethyl *5,3',5'-triethyl myricetin to ω,4-dimethoxy-2-ethoxy-6-hydroxy acetophenone* (4) *and 3,5-diethyl-4-methyl gallic acid* : A solution of 3,7,4'-trimethyl-5,3',5'-triethyl myricetin (0.5 g) in ethanolic NaOH (3 *N* ; 70 ml) was refluxed on water bath for 1 hr. The solvent from the reaction mixture was removed by evaporation, the residue diluted with water, acidified with dil. H_2SO_4 (6 *N*) and extracted with ether. The ether extract was washed several times with aq. $NaHCO_3$ and then with water, dried and evaporated to give a phenolic solid (0.09 g) which crystallised from methanol as colourless needles of 4, $C_{12}H_{16}O_5$, (M^+, 240), m.p. 95° ; ^1H nmr : δ 3.55 and 3.85 (3H, *s* each, R-OMe and Ar-OMe), 1.5 (3H, *t*, $-OCH_2CH_3$), 1.45 (2H, *q*, $-OCH_2CH_3$), 5.92 and 6.12 (1H, *d* each, J=2.5 Hz, C-3 and C-5 H), 4.7 (2H, *s*, $-COCH_2OCH_3$), 13.85 (1H, *br*, chelated ArOH) ; MS : m/e 240 (M^+), 195 (M^+-CH_2OMe), 167 (M^+-$COCH_2OMe$). Found : C, 59.72 ; H, 6.85. $C_{12}H_{16}O_5$ requires C, 59.99 ; H, 6.71%.

The combined bicarbonate washings of the above ether extract was acidified and extracted with ether. The ether extract was washed, dried and evaporated to dryness to give a solid (0.12 g) which crystallised from petrol (60-80°) as needles of 3,5-diethyl-4-methyl gallic acid, m.p. 108° ; ^1H nmr : δ 3.90 (3H, *s*, -OMe), 1.40 (6H, *t*, J=7 Hz) and 4.20 (4H, *q*, J=7 Hz, 2-OEt), 7.40 (2H, *s*, C-2 and C-6 H), 10.6 (1H, *br*, CO_2H), identical with synthetic sample[6] of 3,5-diethyl-4-methyl gallic acid (m.m.p., ir).

3,7,3',4'-Tetramethylmyricetin crystallised from MeOH as pale yellow needles, $C_{19}H_{18}O_8$, m.p. 148-50° (Lit.[7] m.p. 149-51°). Found : C, 60.73 ; H, 4.74. $C_{19}H_{18}O_8$ requires C, 60.96 ; H, 4.85%. It gave a diacetate, m.p. 185-86° ; ^1H nmr : δ 2.35 and 2.45 (3H, *s* each, 2-OAc), 3.82, 3.90, 3.95 and 3.96 (3H, *s* each, 4-OMe), 6.58 and 6.78 (1H, *d* each, J=2.5 Hz, C-6 and C-8 H), 7.38 and 7.60 (1H, *d* each, J=2.5 Hz, C-2' and C-6' H) ; MS : m/e 374 (M^+) 360, 359, 331, 167.

Selective methylation of quercetin to 3,7,4'-trimethylquercetin (2, R=R₂=H, R₁=Me) and 3,7,3',4'-tetramethylquercetin (2, R=H, R₁=R₂=Me) : Methylation of quercetin (2 g) with Me_2SO_4 in presence of $NaHCO_3$ and subsequent chromatography of the reaction mixture furnished trimethylquercetin (0.96 g) and tetramethylquercetin (0.36 g).

3,7,4'-Trimethylquercetin crystallised from MeOH as yellow microneedles, $C_{18}H_{16}O_7$, m.p. 174° (Lit.[8] m.p. 172-73°). Found : C, 62.58 ; H, 4.90. $C_{18}H_{16}O_7$ requires C, 62.79 ; H, 4.68%. It gave a diacetate, m.p. 173-75° ; ^1H nmr (90 MHz) : δ 2.35 and 2.45 (3H, *s* each, 2-OAc), 3.80, 3.89, 3.91 (3H, *s* each, 3-OMe), 6.61 and 6.83 (1H, *d* each, J=2 Hz, C-6 and C-8 H), 7.08 (1H, *d*, J=9 Hz, C-5' H), 7.81 (1H, *d*, J=2 Hz, C-2' H), 8.05 (1H, *dd*, J_1=9 Hz, J_2=2 Hz, C-6' H). Found : C, 61.54 ; H, 4.95. $C_{20}H_{20}O_9$ requires C, 61.68 ; H, 4.71%. MS : m/e 344 (M^+), 330, 329, 315, 301, 287.

Ethylation of 3,7,4'-trimethylquercetin followed by alkali hydrolysis *in situ* gave the acetophenone (4) and O-ethylisovanillic acid, m.p. 164° (Lit.[9] m.p. 165-66°).

3,7,3',4,-Tetramethylquercetin crystallised from MeOH as pale yellow needles, $C_{19}H_{18}O_7$, m.p. 158° (Lit.[10] m.p. 159-60°). Found : C, 63.53 ; H, 4.89. $C_{19}H_{18}O_7$ requires C, 63.68 ; H, 5.06%. MS : m/e 358 (M^+), 344, 343, 329, 313, 301. It gave colourless crystals of monoacetate, $C_{21}H_{20}O_8$, m.p. 168-69° ; ^1H nmr (90 MHz) : δ 2.46 (3H, *s*, -OAc), 3.80, 3.91, 3.98 (3H, 3H and 6H, *s* each, 4-OMe), 6.62 and 6.83 (1H, *d* each, J=2.5 Hz, C-6 and C-8 H), 7.00 (1H, *d*, J=9 Hz, C-5' H), 7.67 (1H, *d*, J=2 Hz, C-2' H), 7.72 (1H, *dd*, J_1=9 Hz, J_2=2 Hz, C-6' H). Found : C, 62.99 ; H, 4.83. $C_{21}H_{20}O_8$ requires C, 62.99 ; H, 5.04%.

Methylation of quercetin with Me₂SO₄ in presence of NaOAc to 7,4'-dimethylquercetin (3) : Methylation of quercetin (1 g) with Me_2SO_4 in dry acetone in presence of NaOAc (instead of $NaHCO_3$) gave 7,4'-dimethyl quercetin (0.56 g) as bright yellow needles, $C_{17}H_{14}O_7$, m.p. 230-31° (Lit.[11] m.p. 229-30°), λ_{max} (MeOH) 255, 305 sh, 367 nm (log ε, 4.39, 3.93, 4.38) ; λ_{max} (MeOH/NaOAc) 255, 305, 367 nm ; λ_{max} (MeOH/NaOAc/H_3BO_3) 255, 305 sh, 367 nm ; ν_{max} (KBr) : 3280, 3450, 1655, 1618 cm^{-1} ; ^1H nmr (90 MHz) : δ 3.86 and 3.99 (3H, *s* each, 2-OMe), 6.30 and 6.58 (1H, *d* each, J=2.5 Hz, C-6 and C-8 H), 7.05 (1H, *d*, J=9 Hz, C-5' H), 7.77

(2H, *m*, C-2′ and C-6′ H); MS: m/e 330 (M^+), 315, 301, 287, 259, 231, 149, 135. Found: C, 62.11; H, 4.26. $C_{17}H_{14}O_7$ requires C, 61.81; H, 4.24%.

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Thiocarbamide as Dealkylating Agent: Debenzylation of Certain 2-S-Benzyl-1,5-diaryl-2,4-isodithiobiurets with Thiocarbamide

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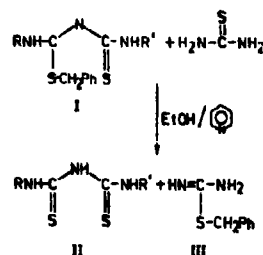
APPLICATION of thiocarbamide as debenzylating agent for 1-aryl-S-benzyl isothiocarbamides in acid medium was reported earlier[1]. It is of interest to investigate this debenzylation reaction in other S-benzylated thioamido systems like 2-S-benzyl-1,5-diaryl-2,4-isodithiobiurets (I). With this end in view, debenzylations of I have been attempted in basic and acidic conditions. No debenzylation is observed in acid medium. However, smooth debenzylation reaction of I is observed in presence of a tertiary base like pyridine. The present note describes these observations.

The debenzylation reaction of 2-S-benzyl-1,5-diphenyl-2,4-isodithiobiuret (**Ia**) with thiocarbamide in presence of pyridine in boiling ethanolic medium affords a product, m.p. 143°. Elimination of hydrogen sulphide is not observed during the reaction. The product is desulphurisable when boiled with alkaline plumbite solution. On pyrolysis, it gives a distinct odour of phenyl isothiocyanate. The ir spectrum of the product clearly indicates the presence of ν(NH) (3300 cm^{-1}), ν(C=S) (1210 cm^{-1}) and ν(C−S) (705 cm^{-1}) bands[2]. No depression in melting point is observed when it is mixed with an authentic sample of 1,5-diphenyl-2,4-dithiobiuret (**IIa**)[3]. On the basis of all these facts, the product with m.p. 143° has been assigned structure **IIa**. In this reaction, S-benzyl isothiocarbamide (**III**) has been isolated as its picrate derivative, m.p. 181°.

Other 2-S-benzyl-1,5-diaryl-2,4-isodithiobiurets (**Ib** and **Ic**) also get debenzylated into the related 1,5-diaryl-2,4-dithiobiurets (**IIb** and **IIc**) under analogous reaction conditions.

RNH–C(–SCH$_2$Ph)=N–C(=S)–NHR′ (I) + H$_2$N–C(=S)–NH$_2$

↓ EtOH / pyridine

RNH–C(=S)–NH–C(=S)–NHR′ (II) + HN=C(–S–CH$_2$Ph)–NH$_2$ (III)

where R = (a) phenyl, (b) *p*-chlorophenyl and (c) *m*-chlorophenyl and R′ = phenyl.

Experimental

The required 2-S-benzyl-1,5-diaryl-2,4-isodithiobiurets (I) have been prepared by the interaction of 1-aryl-S-benzyl isothiocarbamides[4] and aryl isothiocyanates by a known procedure[5] (**Ib**, m.p. 120° and **Ic**, m.p. 102° have been prepared for the first time).

Debenzylation of 2-S-benzyl-1,5-diaryl-2,4-isodithiobiurets (I); *Formation of 1,5-diaryl-2,4-dithiobiurets* (II): Details of a typical experiment (where aryl = phenyl) are as follows:

2-S-benzyl-1,5-diphenyl-2,4-isodithiobiuret (**Ia**, 2g) is suspended in ethanol (20 ml) and thiocarbamide (0 4 g) and pyridine (1 ml) are added to this. The reaction mixture is refluxed for 3 hr. Neither hydrogen sulphide nor benzyl mercaptan is eliminated. The reaction mixture is then cooled and acidified with dilute aqueous hydrochloric acid when an oily mass is obtained. The clear supernatent liquid is decanted off and to this is added an aqueous solution of picric acid when a yellow product is obtained. This is filtered and crystallized from ethanol, m.p. 181°. It is identified as the picrate of S-benzyl isothiocarbamide (III).

The oily mass is washed thoroughly with water and then triturated several times with petroleum ether followed by ethanol when a yellow solid

(1.7 g) is obtained. It is crystallized from ethanol, m.p. 143° (Found : N, 14.93 ; S, 21.53. $C_{14}H_{13}N_3S_2$ requires N, 14.63 ; S, 22.30%). This has been identified as 1,5-diphenyl-2,4-dithiobiuret (IIa) on the basis of m m.p. with an authentic sample[5].

When the debenzylations of other 2-S-benzyl-1,5-diaryl-2,4-isodithiobiurets (Ib and Ic) were carried out with thiocarbamide in presence of pyridine in an ethanolic medium, the related products were obtained (IIb, m.p. 156° ; Found : N, 13.56 ; S, 19.25. $C_{14}H_{12}N_3S_2Cl$ requires N, 13.06 ; S. 19.91% and IIc, m.p. 145° ; Found : N, 13.26 ; S, 20.34. $C_{14}H_{12}N_3S_2Cl$ requires N, 13.06 ; S, 19.91%).

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Some Interesting Reactions of N-Phenyl-S-chloro isothiocarbamoyl Chloride

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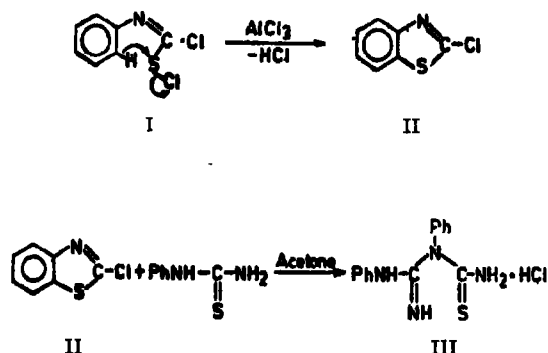
CHEMISTRY of N-phenyl-S-chloro isothiocarbamoyl chloride (I) with special reference to its application as an important intermediate in heterocyclic synthesis has been exhaustively investigated in this laboratory. The present note describes the intramolecular reaction of I in presence of anhydrous aluminium trichloride and intermolecular reaction in presence of aqueous ethanol and mixture of chloroform and aqueous ethanol in different proportions.

When N-phenyl-S-chloro isothiocarbamoyl chloride is boiled with anhydrous aluminium trichloride in dry diethyl ether medium for 4 hr evolution of hydrogen chloride is observed. The reaction mixture on fractional distillation gives an oily product, b.p. 248°. It is identified as 2-chlorobenzothiazole (II) on the basis of its reaction with phenyl thiocarbamide in acetone medium when 1-(phenylformamidino)-1-phenyl thiocarbamide hydrochloride (III), m. p. 158° is isolated[1]. The formation of 2-chlorobenzothiazole (II) may be explained as follows :

I —($AlCl_3$, −HCl)→ II

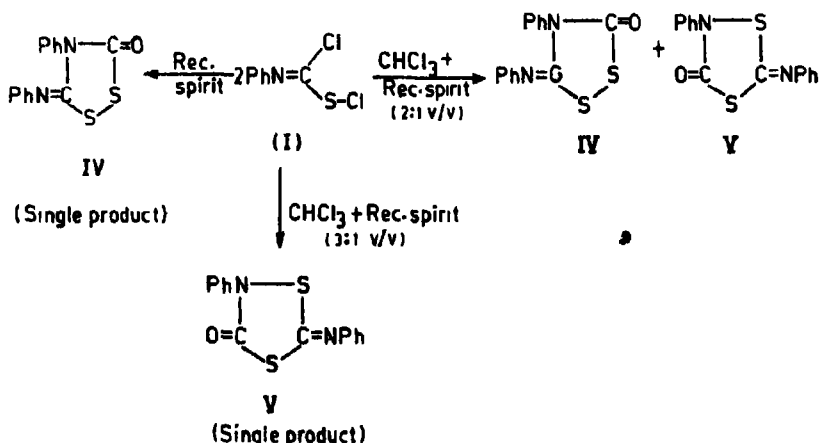
II + PhNH–C(=S)–NH_2 —(Acetone)→ PhNH–C(=NH)–N(Ph)–C(=S)–NH_2·HCl

II III

When rectified spirit is added to a chilled N-phenyl-S-chloro isothiocarbamoyl chloride (I) solution with stirring, a pale yellow solid, m.p. 118° is obtained. It is identified as 3-oxo-4-phenyl-5-phenylimino-1,2,4-dithiazolidine (IV) on the basis of m.m p. with an authentic sample[3].

When the same reaction of I is carried out with a mixture of chloroform and rectified spirit (1 : 1, v/v), only IV is obtained. However, the reaction of I with a mixture of chloroform and rectified spirit (2 : 1, v/v) gives IV and also 5-oxo-4-phenyl-2-phenylimino-1,3,4-dithiazolidine (V). The latter has been identified on the basis of m.m.p. with an authentic sample[3]. As the ratio of chloroform in the mixture of chloroform and rectified spirit is increased, (3 : 1, v/v), V is formed almost exclusively. The IV and V may form as shown below.

2PhN=C(Cl)–S–Cl (I) —(Rec. spirit)→ IV (Single product)

(I) —($CHCl_3$ + Rec. spirit, 2:1 v/v)→ IV + V

(I) —($CHCl_3$ + Rec. spirit, 3:1 v/v)→ V (Single product)

No definite reaction mechanism could be established for the formation of IV and V. However, it is almost clear that the ratio of IV and V formed is dependant upon the concentration of rectified spirit. In presence of higher concentration of rectified spirit, more of IV is formed while in lower concentration of rectified spirit, V is the major product.

Experimental

The required N-phenyl-S-chloro isothiocarbamoyl chloride (I) has been prepared as usual[4].

Intramolecular cyclisation of N-phenyl-S-chloro isothiocarbamoyl chloride (I) *in presence of anhydrous aluminium trichloride ; Formation of 2-chlorobenzothiazole* (II) *:*

Anhydrous aluminium trichloride (16 g) is gradually added to an ice cold solution of I in dry diethyl ether (0.1 *M* ; 21 g in 75 ml), maintaining the temperature at $-5°$. After complete addition, the reaction mixture is allowed to stand for 30 min below 10° and then refluxed for 3 hr. It is then cooled and crushed ice ($\sim$100 g) is gradually added to decompose the probable aluminium trichloride complex. The resultant oily mass separated at the bottom is repeatedly extracted with diethyl ether. The ethereal solution on fractional distillation gives a fraction collected at 245-248° in the form of a viscous oily liquid (Found : N, 8 48 ; S, 18.02. C_7H_4NSCl requires N, 8.26 ; S, 18.88%). It is identified as 2-chlorobenzothiazole (II) on the basis of its interaction with phenyl thiocarbamide in acetone medium, when 1-(phenylformamidino)-1-phenyl thiocarbamide hydrochloride (III), m.p. 158° is obtained (Found : N, 18.31 ; S, 9.88. $C_{14}H_{14}N_4SCl$ requires N, 18 23 ; S, 10.42%). The latter also gives picrate, m.p. 142°. Both these products are identified on the basis of m.m.p. with authentic samples[1].

Intermolecular condensation of N-phenyl-S-chloro isothiocarbamoyl chloride (I) *. Formation of 3-oxo-4-phenyl-5-phenylimino-1,2,4-dithiazolidine* (IV) and *5-oxo-4-phenyl-2-phenylimino-1,3,4-dithiazolidine* (V) *:*

(a) *Reaction in aqueous ethanol :* N-Phenyl-S-chloro isothiocarbamoyl chloride (I) (0.1 *M* ; 21 g) is cooled to 0° and chilled aqueous ethanol (25 ml) is added. An extremely vigorous and exothermic reaction is observed and almost immediately a pale yellow solid separates out. It is filtered, washed with a little ethanol and crystallized from glacial acetic acid, m.p. 118° (Found : N, 9.88 ; S, 21.92. $C_{14}H_{10}N_2S_2O$ requires N, 9.79 ; S, 22.39%). It is identified as 3-oxo-4-phenyl-5-phenylimino-1,2,4-dithiazolidine (IV) on the basis of m.m.p. with an authentic sample[3].

(b) *Reaction in a mixture of aqueous ethanol-chloroform (1 : 1, v/v) :* To N-phenyl-S-chloro isothiocarbamoyl chloride (21 g) is gradually added a mixture of chloroform aqueous ethanol (1 : 1, v/v ; 50 ml) at 0°. A vigorous exothermic reaction, accompanied by evolution of hydrogen chloride is observed and almost immediately a pale yellow solid separates out. It is filtered, washed with a little aqueous ethanol and crystallized from glacial acetic acid, m.p. 118° (Found : N, 10.05 ; S, 22.55. $C_{14}H_{10}N_2S_2O$ requires N, 9.79 ; S, 22.39%). It is identified as 3-oxo-4-phenyl-5-phenylimino-1,2,4-dithiazolidine (IV) on the basis of m.m.p. with an authentic sample[3].

(c) *Reaction in a mixture of aqueous ethanol-chloroform (1 : 2, v/v) :* To an ice cold N-phenyl-S-chloro isothiocarbamoyl chloride (21 g) is added a chilled mixture (75 ml) of chloroform-aqueous ethanol (2 : 1, v/v) when a vigorous reaction is noticed and a pale yellow solid separates out. It is filtered, washed with a little aqueous ethanol and crystallized from glacial acetic acid, m.p. 118°. It is identified as 3-oxo-4-phenyl-5-phenylimino-1,2,4-dithiazolidine (IV) as usual.

The filtrate, on addition of petroleum ether, affords a semisolid mass which on trituration several times with petroleum ether followed by ethanol is converted into a pale yellow solid, crystallized from glacial acetic acid/benzene/chlorobenzene, m.p. 245° (Found : N, 9.82 ; S, 22.45. $C_{14}H_{10}N_2S_2O$ requires N, 9.79 ; S, 22.39%). It is identified as 5-oxo-4-phenyl-2-phenylimino-1,3,4-dithiazolidine (V) on the basis of m.m.p. with an authentic sample[3].

(d) *Reaction in a mixture of aqueous ethanol-chloroform (1 : 3, v/v) :* To N-phenyl-S chloro isothiocarbamoyl chloride (21 g) is added a mixture (100 ml) of aqueous ethanol-chloroform (1 : 3, v/v) at 0 and the reaction mixture is allowed to stand below 10° for about 30 min. A very mild reaction is noticed. The reaction mixture is then allowed to stand for 3 hr at room temperature and treated with excess petroleum ether when a semisolid mass is obtained. This, on trituration several times with petroleum ether followed by ethanol, affords a pale yellow solid crystallized from glacial acetic acid, m.p. 245°. This is identified as 5-oxo-4-phenyl-2-phenylimino-1,3,4-dithiazolidine (V) on the basis of m.m p. with an authentic sample[3].

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Studies on 2-pyrazolin-5-one Derivatives

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In our earlier communications, we reported that 5-pyrazolone[1-4] and its derivatives, 4-acetyl-2-pyrazolin-5-one[5] and 2-pyrazolin-5-thione[6], were

associated with significant fungicidal activity against the rice blast pathogen *Pyricularia oryzae* and brown leaf spot pathogen *Helminthosporium oryzae*. Fungicidal property[6,7] has been noted in 2-mercapto-3-aryl-4-thiazolidone and 2-pyrazolin-5-thione. It was therefore considered worthwhile to synthesise a new heterocyclic compound containing both the fungicidally active moieties, pyrazolone and thiazolidone.

4-Acetyl-1-phenyl-3-methyl-2-pyrazolin-5-one condensed at the active methyl site of 2-mercapto-3-aryl-4-thiazolidone in ethanol to afford the compound [2-(1-phenyl-3-methyl-2-pyrazolin-5-one-4-yl)-2-(2′-mercapto-3′-aryl-4′-thiazolidone-5′-ylidene)-ethane]. The structure of the compound was established from analytical data and ir spectra. The ir spectra of the compound indicate the characteristic band at 1740 cm^{-1} for ring (>C=O), weak band at 2990 cm^{-1} for heterocyclic –CH stretching vibration, band at 1490 cm^{-1} for $-CH_2$ bonding vibration, and at 1590, 1050, 750 cm^{-1} attributed to –C=N, –C=S, >C–S–C< stretching vibrations, respectively.

1-Phenyl-3-methyl-2-pyrazolin-5-thione condensed at the 5 position with phenacyl bromide in presence of ethanol and fused sodium acetate to yield 5-ether product of 1-phenyl-3-methyl-2-pyrazolin-5-thione and phenacyl bromide. It does not dissolve in 10% aq. alkali and does not give any colouration with alcoholic $FeCl_3$ solution.

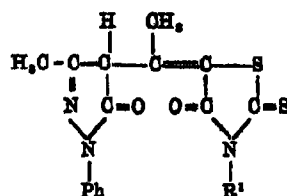
The ir data indicate the absence of enolic band. Band at 1680 cm^{-1} indicates the presence of characteristic exocyclic carbonyl group absorption, aromatic nucleus at 1370 cm^{-1} and hydrogen atoms of mono-substituted aromatic nucleus at 760 and 740 cm^{-1}. From nmr data in $CDCl_3$ it has been noted that peaks at δ2.2 comes as singlet for 3H of one methyl group, δ3.9 indicates a singlet for 2H, δ6.15 comes as singlet of 1H at C_4 position. Also, a multiplet in between δ7.4-δ7.9 indicates the presence of phenyl group. The molecular weight of this compound has been determined from the mass spectra and found to be 308 (M^+). Peaks at 308, 203, 188, 173, 103, 77, 51 m/e are obtained.

The compounds thus prepared were screened for their antifungal activity against the rice blast pathogen *P. oryzae* and the brown leaf spot pathogen *H. oryzae* by the standard method[8] of spore germination tests at various concentrations. It is found that only one compound (Sl. No. 9, Table 1) is active against both the pathogens. It was of further interest to note that 5 other compounds (Sl. No. 1, 5, 6, 7, 10, Table 1) were active at 1000 ppm. The compound No. 1 in Table 2 is found to be more active than the O-ether product earlier reported by Das and Mittra[9].

Experimental

All melting points are uncorrected. IR spectra were recorded in Infrared spectrophotometer.

TABLE 1

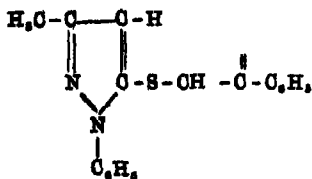
```
          H   CH3
          |   |
H3C - C — C — C ═══ C ——— S
      ‖   |         |     |
      N   C=O   O=C     C=S
       \ /         \   /
        N           N
        |           |
        Ph          R¹
```

Sl. No.	R_1	m.p. °C	%S Found (Calcd.)	% inhibition of germination at 1000 ppm: *P. oryzae*	*H. oryzae*
1.	C_6H_5	167	15.65 (15.72)	62.4	56.8
2.	o-C_6H_4Cl	107	14.62 (14.99)	45.9	36.2
3.	m-C_6H_4Cl	72	14.55 (14.99)	49.6	39.7
4.	p-C_6H_4Cl	101	14.82 (14.99)	50	42.1
5.	o-$C_6H_4OCH_3$	85	11.52 (11.61)	69	40
6.	p-$C_6H_4OCH_3$	169	11.53 (11.61)	55	45
7.	p-$C_6H_4OC_2H_5$	62	14.06 (14.19)	32	27
8.	o-$C_6H_4CH_3$	99	15.16 (15.20)	65.9	56
9.	m-$C_6H_4CH_3$	75	15.35 (15.20)	70.1	61
10	p-$C_6H_4CH_3$	117	15.18 (15.20)	61	52.6

General method for the preparation of 2-(1-phenyl-3-methyl-2-pyrazolin-5-one-4-yl)-2-(2′-mercapto-3′-aryl-4′-thiazolidone-5′-ylidene) ethane : A solution of 1-phenyl-3-methyl-4-acetyl-2-pyrazolin-5-one (0.01 mole) and 2-mercapto-3-aryl thiazolidone (0.01 mole) in ethanol (20 ml) was added dropwise to 40% NaOH (15 ml) and allowed to stand overnight. It was then refluxed for 1 hr on a water bath. Excess of the solvent was removed and the resulting solution was acidified with dil. acetic acid. An yellow solid mass separated which was filtered, washed with water and finally crystallised from ethanol.

Procedure for the synthesis of S-ether product of 2-pyrazolin-5-thione and phenacyl bromide : 1-Phenyl-3-methyl-2-pyrazolin-5-thione (1.9 g) and phenacyl bromide (1.9 g) were taken in ethanol (10 ml) followed by fused sodium acetate (3 g) and was refluxed for 2 hr on a water bath. Excess ethanol was evaporated and cooled and water added. The brown compound thus isolated was then dissolved in 10% aqueous sodium hydroxide solution. It was allowed to stand at room temperature for 1 hr and filtered. The filtrate and the residue were collected separately. The filtrate was acidified with dil. HCl when no product was obtained. The residue was repeatedly washed with water and dried. It was then recrystallised from ethanol. A cream coloured product was obtained, m.p. 49°, yield 60%.

The compound is insoluble in 10% aqueous sodium hydroxide solution and does not give any colouration with alcoholic ferric chloride solution.

TABLE 2

H_3C-C — $C-H$; N, N (pyrazole ring) ; $C-S-CH$; $-\overset{O}{\overset{\|}{C}}-OC_2H_5$; $N-C_6H_5$

Sl. No.	m.p. °C	%S Found (Calcd.)	%inhibition of germination at 1000 ppm	
			P. oryzae	*H. oryzae*
1.	47	10.54 (10.88)	70	48

Acknowledgement

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Flavonoids and other Constituents of *Indigofera hetrantha*

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THE plant *Indigofera hetrantha* (wild) belonging to Leguminosae was collected from Gulmarg, Kashmir in June and was identified in the herbarium of the Botany Department, Kashmir University. The sister species of *Indigofera hetrantha* were found to contain toxic nitro compounds[1,2] of insecticidal activity[3]. It was, therefore, considered worthwhile to investigate this plant for its chemical composition.

Experimental

The dried plant material (12 kg) was extracted by percolation with ethanol. After removal of the solvent *in vacuo* at 40° the residue (100 g) was partitioned between 2% aq. citric acid and ether to give a basic and a non-basic fraction. The non-basic fraction was fractionated by standard methods into neutral (20 g), acidic (15 g) and phenolic (6 g) fractions.

The phenolic fraction was chromatographed over silica gel (60-100 mesh). Elution with $CHCl_3$, $CHCl_3-MeOH$ afforded IH_4, IH_5 and IH_6 which were purified by re-column chromatography and preparative paper chromatography (Whatman No. 3, 15% HOAc).

The acidic fraction on chromatography over silica gel using $C_6H_6-CHCl_3$ (1 : 3) as the eluent gave IH_7 which was purified by recrystallization.

The neutral fraction on chromatography over silica gel using light petrol, petrol-C_6H_6, C_6H_6 as the eluents afforded IH_1, IH_2 and IH_3.

Refrigeration of acidic solution of the basic fraction gave an alkaloidal precipitate (300 mg). The tlc examination of this fraction revealed the presence of several compounds but could not be worked further because of the small amount.

Results

IH_4 : Yellow needles, m.p. 347-8°, M^+, 270 agreed with elemental analysis of $C_{15}H_{10}O_5$. The compound was identified as apigenin[4] by uv, ir, nmr, m.m.p. The structure was further confirmed by its conversion to tri-acetate, m.p. 186°.

IH_5 : Yellow needles crystallized from EtOH, m.p. 261°, M^+, 284 agreed with elemental analysis of $C_{16}H_{12}O_5$. The compound was identified as acacetin[5,6] by co-tlc, m.m.p. and superimposable ir. Acetylation with Ac_2O/py gave a di-acetate, m.p. 203-5° further confirming its structure.

IH_6 : Yellow needles, m.p. 234-6°, M^+, 464. The compound was isolated by preparative paper chromatography and gave an olive-green colouration with $FeCl_3$. It was identified as isoquercitrin[7] by uv, ir, nmr and m.m.p. On acid hydrolysis it gave quercitin[8], m p. 313-16° and glucose confirming its structure.

IH_7 : It was identified as ursolic acid[10] (150 mg), m.p. 242-4°. Its ir in KBr pellet showed the following absorption bands : ν_{max} 3450, 2950, 2890, 1685, 1450, 1030 and 990 cm^{-1}. MS M^+, 456. Treatment with Ac_2O/py gave O-acetyl ursolic acid, m.p. 268-270°. Direct comparison (m.p., m.m.p, ir) with an authentic sample confirmed the identity.

IH_1 and *IH_2* could dot be processed further due to their small amounts.

IH_3 : A white crystalline solid, m.p. 135-6°, was found to be β-sitosterol[9] by co-tlc and m.m.p.

This appears to be the first record of the isolation of these compounds from this species.

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Chemical Constituents of *Eucalyptus citriodora* Roots

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EUCALYPTUS citriodora (F : Myrtaceae) is distributed[1] in India, Australia and many other countries. An essential oil (0.5-2.0%) is obtained from its leaves which is used in soap perfumery and as a source of citronellal. Eucalyptus[2] is used in the treatment of catarrhal states of bronchopulmonary mucous membrane, intermittent and septic fevers, diphtheria, whooping cough etc. Earlier examination showed the presence of oil and flavonoids in the leaves[3-6] while the gum[7] contained ellagic acid and flavonoids.

The present note deals with the chemical examination of the roots of *Eucalyptus citriodora*. The roots (3 kg) were extracted with hot acetone and alcohol separately. The acetone extract, on column chromatography over silica gel, gave six compounds (**A**–**F**). Compound **A** (β-sitosterol) crystallised from chloroform-methanol as colourless needles (50 mg), m.p. 136°, $[\alpha]_D -34.5°$ ($CHCl_3$). Co-TLC and m.m.p. with an authentic sample confirmed its identity[8]. Compound **B** (Betulinic acid) crystallised from methanol as silky needles (500 mg), m. p. 312-14°, $[\alpha]_D +9°$ ($CHCl_3$). It responded to L.B. test and formed an acetate, m. p. 286-88°. Identity established by m.m.p. with an authentic sample of betulinic acid[9], co-tlc and superimposable ir.

Compound **C** (ursolic acid) crystallised from methanol as colourless needles (200 mg), m. p. 288-90°, $[\alpha]_D +69°$ ($CHCl_3$) and gave +ive L. B. test (pink→blue). Acetate, m. p. 245-46°, $[\alpha]_D +57°$ ($CHCl_3$). It was identified as ursolic acid[10] by m.m.p., co-tlc and superimposable ir.

Compound **D** (7-O-methylaromadendrin) crystallised from $CHCl_3$-MeOH as light pale flat needles (2.0 g), m.p. 187-88°, $[\alpha]_D +30°$ (MeOH) and gave a transient purple to brown colour with $FeCl_3$ and +ive Zn/HCl test. Acetate, m.p. 136-37° (M^+ 428). It resembled in all respect with authentic 7-O-methylaromadendrin[7] (ir, uv, nmr and mass). Compound **E** (aromadendrin) crystallised from methanol-benzene as colourless needles (800 mg), m.p. 247-48°, $[\alpha]_D +25.5°$ (MeOH) (M^+ 288) Acetate, m.p. 80-82°. It was characterised as aromadendrin[7] by ir, uv, nmr, mass and by direct comparison with an authentic sample (co-tlc, m.m.p.). Compound **F** (fustin) obtained as colourless solid from ethyl acetate-petroleum ether (250 mg), m.p. 213-15°, gave green colour with $FeCl_3$ and +ive Zn/HCl test. Acetate, m p. 149-51°. It was identified as fustin[11] by ir, uv, nmr and by direct comparison with an authentic sample (co-tlc and m.m.p.).

Thus the occurrence of β-sitosterol, betulinic acid, ursolic acid, aromadendrin and 7-O-methylaromadendrin is noted for the first time in the roots of a Eucalyptus species and fustin for the first time in Eucalyptus.

No single compound could be isolated from alcohol extract.

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Systematic Study of the Solvent Extraction of Metal-Tridentate Schiff Base Complexes

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GENERAL surveys of the solvent extraction of metals by oxine[1] (8-hydroxy quinoline), β-diketones[2] and N-benzoyl-N-phynyl hydroxylamine[3] have been published. However, there has been no systematic study of solvent extraction of metals by Schiff base ligands. A general study of over twenty-five metal ions with salicylidene amino thiophenol has been carried out to assess the utility of this type of ligands in the solvent extraction. Schiff base ligands form strong complexes with several metals and as such are expected to be attractive as chelating ligands in extraction work.

Experimental

Reagents. All reagents used were of A. R. quality. Benzene (A.R.) was used as such without any further purification.

Preparation of 2-salicylidene amino thiophenol : The ligand was prepared by mixing *o*-amino thiophenol (Koch Light) and salicylaldehyde (England) in the ratio of 1 : 1 in benzene solution. The ligand separated out after 2 hr. It was filtered under suction. The ligand was recrystallised from benzene. Its melting point was found to be $135^\circ \pm 2^\circ$.

Buffer solution : Perchloric acid, sodium perchlorate and sodium hydroxide mixtures were used as buffer between *p*H 2-4, acetic acid and ammonia mixtures for the *p*H range 4-8 and ammonium chloride ammonia mixtures for the *p*H range 8-10.

Instrumental measurements. Measurements of *p*H were made using Elico *p*H meter standardised with standard buffer solutions of *p*H 4 and 7. The accuracy of the instrument was ± 0.05 *p*H units. In every case, the *p*H of the aqueous phase was measured after the extraction. For spectrophotometric measurements, Bausch and Lomb spectrophotometer (Spectronic-20) was employed. The spectrophotometric measurements are reproducible to ± 0.01 absorbance unit. A calibration curve for each metal was obtained by using known concentrations of the metal and the unknown concentration of a metal was calculated from its respective calibration curve.

Procedure for solvent extraction : A solution of salicylidene amino thiophenol (10 ml of 1×10^{-3} *M*) in chloroform was added to an equal volume of an aqueous phase containing the appropriate metal and buffer in a glass stoppered bottle and shaken in wrist type mechanical shaker. All experiments were carried out at $30\pm2^\circ$. The total ionic strength of the aqueous phase was kept constant at 0.1 *M*. The equilibration time was 3 hr unless otherwise specified. After the equilibrium had been reached, the two phases were separated and the concentration of the metal ion in the aqueous phase was determined spectrophotometrically The distribution ratio (or per cent extraction) was then calculated from the known concentration of the metal, (1.0×10^{-4} *M*) and from the equilibration concentration of the metal in aqueous phase. The metal content in the organic phase was calculated by difference. The distribution ratio was calculated according to the following relationship .

$$D_0 = \frac{\text{Total metal concentration in the organic phase}}{\text{Total metal concentration in the aqueous phase}}$$

Attainment of the extraction equilibrium : The rate of attainment of the equilibrium depends upon many factors Primarily, it depends on the properties of the metal under investigation. Achievement of the equilibrium also depends on the *p*H and the concentration of the ligand. In general, it may be said that the rate of extraction increases with increasing *p*H values, irrespective of the ligand concentration. It is also observed that the rate of extraction increased with increase of equilibration time. Therefore, the equilibration time was kept at 3 hr for most of the metals unless otherwise specified.

All the metal extractions were carried out keeping the ligand concentration at 1×10^{-3} *M* and varying the *p*H of the aqueous phase from 2-10. The ligand dissolution took place at a *p*H higher than 10. Ishii has reported that nickel(II)[4] and zinc(II)[5] can be quantitatively extracted in the neutral or alkaline medium. It was thought worthwhile to carry out systematically the metal extraction studies at varying *p*H.

From the results obtained, the metals can be divided into the following three categories based on their extraction behaviour with salicylidene amino thiophenol

(A) Metals which are quantitatively extracted under certain *p*H ranges.

(B) Metals with the maximum percentage extraction of 50% and above but less than 100%.

(C) Metals with the maximum percentage extraction of less than 50%.

(A) *Metals which are quantitatively extracted under certain* pH *ranges* The metals studied in this category are lead(II), cadmium(II), mercury(II), cobalt(II), nickel(II), zinc(II), cerium(IV) and vanadium(V). All the above metals can be quantitatively extracted under proper conditions as shown in Fig. 1. Extraction of all these metals is sensitive to *p*H and rigorous control over *p*H is necessary for complete extraction.
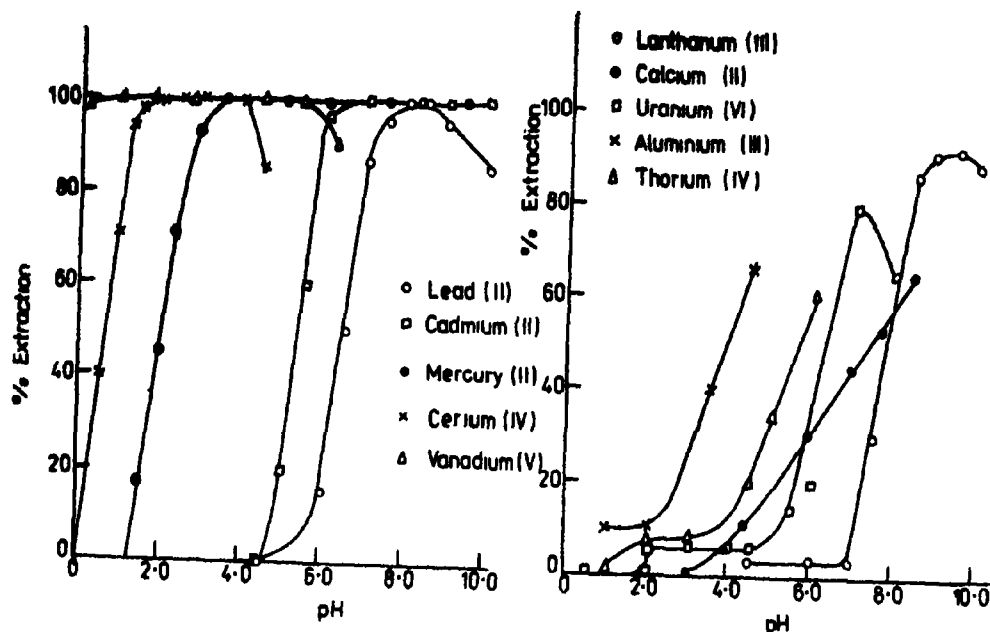
Fig. 1

Fig. 2

Extraction curves for metal - salicylidene aminothiophenol
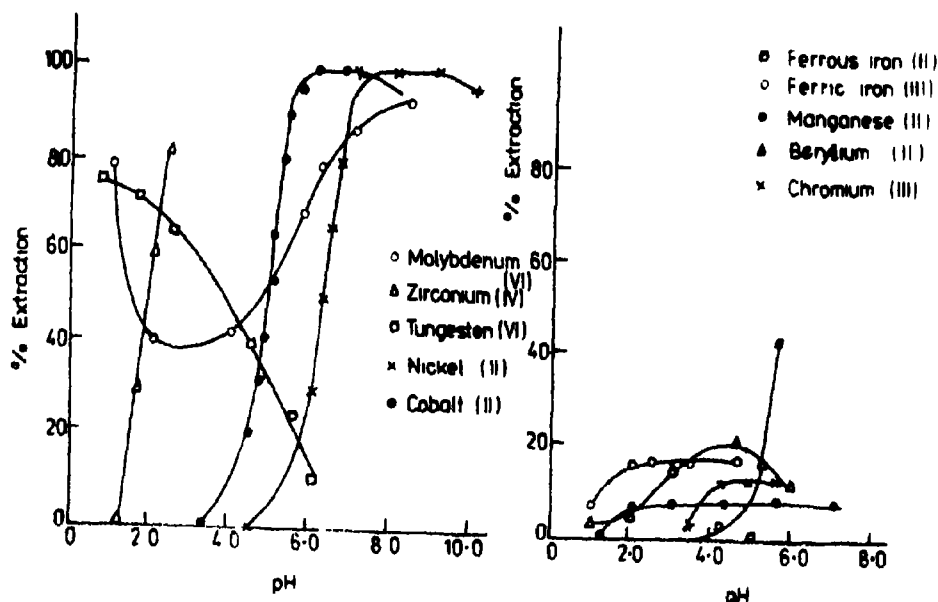
Fig 3

Fig. 4

Extraction curves for metal – salicylidene aminothiophenol

Lead(II) : The extraction of lead(II) started from pH 6.0 and complete extraction took place from pH 8.0-8.5. The extraction decreased from pH 9.0 and above.

Cadmium(II) : The extraction started from pH 5.0 and complete extraction took place between pH 7.0 and 10.0. Extraction and spectrophotometric determination of cadmium(II) seem to be attractive. Precipitation was observed at pH higher than 10.0.

Mercury(II) and vanadium(V) : Both these metals were extracted completely from pH 3.5 to 8.5 and 1.0 to 4.5, respectively. The extraction of vanadium(V) decreased above pH 5.5.

Cerium(IV) · The complete extraction took place between pH 2.0 and 4.0 and the extraction decreased above pH 4.0.

Cobalt(II), nickel(II) and zinc(II) : Nickel(II) and zinc(II) can be extracted and estimated spectro-

photometrically as already reported[4]. Present studies also confirm the data reported in the literature. Cobalt(II) also can be extracted quantitatively in the pH range 5.5 to 7.3.

(B) *Metals with the maximum percentage extraction of 50% and above but less than 100% :* The metals in this category are calcium(II), lanthanum(III), aluminium(III), thorium(IV), zirconium(IV), uranium(VI), molybdenum(VI) and tungsten(VI)

The *p*H extraction curves are given in Figs. 2 and 3, from which it is clear that the metal extraction increases as the *p*H increased except in the case of molybdenum(VI) and tungsten(VI) Tungsten(VI) extraction decreased as the *p*H increased, perhaps due to the formation of polytungstic acids in the aqueous phase. In the extraction of molybdenum(VI), first the metal extraction decreased up to *p*H 2.0 and then increased as the *p*H increased. This behaviour may be due to the formation of different species of molybdenum at *p*H less than 2 when it exists essentially as H_2MO_4 according to Stary[1], and as some different species at *p*H above 2. In the case of calcium(II), thorium(IV) and aluminium(III), there was initial extraction but above certain *p*H values, there was slight precipitation. Therefore the extraction curves could not be plotted for the entire *p*H range.

(C) *Metals with the maximum percentage extraction of less than 50% :* The metals studied under this category are ferrous and ferric iron, manganese(II), beryllium(II) and chromium(III). The *p*H variation curves of these metals are shown in Fig 4. Even when the equilibration time was prolonged to 12 hr in case of beryllium(II) and chromium(III), no significant extraction took place. In case of manganese(II), colour developed immediately which faded out in a few minutes. In case of iron(II) and iron(III), the spectrophotometric studies could not be performed at *p*H higher than 4.0 as there was precipitation.

Silver(I) : Systematic studies of solvent extraction could not be carried out as the distribution ratios obtained by spectrophotometric methods were not reproducible due to absorption of silver ions on glass vessel. As there was no facility to determine the distribution ratios by radiometric method, the investigations are incomplete.

From the above study it can be seen that salicylidene amino thiophenol would be effective in the solvent extraction of various metals discussed above. Detailed investigations will be published subsequently.

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Detection and Chromatographic Separation of Phenols on Papers Impregnated with Ferric Hydroxide

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THE use of chromatographic papers loaded with amberlite ion exchange resin has been reported by Clark[1] Scant attention has been paid on the chromatography of phenols on papers impregnated with inorganic ion exchangers. Use of papers impregnated with stannic molybdate, has been made in our laboratory for the separation of phenols[2].

Experimental

Preparation of ion exchange papers : Whatman No. 3 paper strips of size 14 × 3 cm were dipped in 0.1 *M* ferric nitrate solution for 15-20 sec and then dried at room temperature. These paper strips were then dipped in 0.1 *M* sodium hydroxide solution for 40-45 sec The excess of reagent was drained off and the strips were dried at room temperature over the filter sheets. These treated strips were washed twice with demineralized water to remove the excess of reagent. Finally, the strips were dried again at room temperature and used as such for chromatography.

Procedure : One or two spots of test solution in ethanol were placed on the paper strip with the help of a glass capillary. The paper was conditioned for 15 min and then solvent was allowed to ascend 11 cm in every case using 20 × 5 cm glass jars.

Results and Discussion

Detection : The colours observed with the phenols are listed below :

β-Hydroxy benzoic acid, *β*-naphthol, vanilline, *p*-nitrophenol, *m*-cresol, *p*-cresol, *o*-nitrophenol, picric acid, phloroglucinol, 4-(4-nitrophenyl)-azo resorcinol, di-(2-hydroxyphenylimino) ethane, 4-chlorophenol and 4-(2-pyridilazo) resorcinol gave yellow spots.

Tannic acid, α-naphthol, pyrogallol, resorcinol, catechol, gallic acid and xylenol gave violet spots.

2,4-Dinitrophenol, phenol, quinol and 8-hydroxy-7-iodoquinoline-5-sulphonic acid gave red spots.

Thymol blue, 1,2,5,8-hydroxyanthraquinone and phenyl fluorone, (9-phenyl-2,3,7-trihydroxy-6-fluorone), appeared as grey spots.

1-Nitroso-2-naphthol and bromocresol gave green spots.

TABLE 1—R_f VALUES OF PHENOLS ON FERRIC HYDROXIDE PAPERS IN WATER, SODIUM NITRATE (1.0 *M*, 0.1 *M*, 0.01 *M*), SODIUM CHLORIDE, ALCOHOL AND ALCOHOL+WATER (1 : 1) SYSTEMS

Sl. No.	Phenol	Water	1 0 *M* $NaNO_3$	0.1 *M* $NaNO_3$	0.01 *M* $NaNO_3$	1.0 *M* NaCl	Alcohol	Alcohol+water (1 : 1)
1.	β-Hydroxy benzoic acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.	Tannic acid	0 00	0.00	0.00	0.00	0.00	0.86	1.00
3	Phloroglucinol	0.00	0 65	0.75	0 72	0.71	0 48	0.75
4.	α-Naphthol	0.50	0.54	0.36	0.36	0.00	0.90	0.72
5.	β-Naphthol	0 00	0.00	0.00	0.00	0.00	0.00	0.00
6.	*p*-Hydroxy benzoic acid	0.00	0 00	0.00	0.00	0 00	0.00	0.00
7.	Pyrogallic acid	0.00	0.00	0.00	0 00	0.00	0.00	0.00
8	2,4-Dinitrophenol	0 31	0 46	0.36	0.34	0.56	0.32	0.27
9	*p*-Nitrophenol	0.81	0 73	0.72	0 72	0.67	0.81	0.63
10	Catechol	0 00	0 00	0 00	0.00	0.00	0.00	0.00
11.	*m*-Cresol	0.09	0 00	0 00	0.00	0 00	0.89	0.00
12.	*p*-Cresol	0.00	0 77	0 45	0.40	0.00	0.97	0.65
13.	Phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14.	Resorcinol	0.00	0.77	0.76	0 72	0.70	0.72	0.86
15.	Gallic acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16.	*o*-Nitrophenol	0 81	0 75	0.79	0.60	0.00	0 45	0.32
17.	1-Nitroso-2-naphthol	0 72	0.00	0.00	0.00	0.00	0.81	0.27
18.	Xylenol	0 81	0.65	0.50	0.45	0.18	0.72	0.81
19.	Quinhydrone	0.00	0.00	0.00	0 00	0.00	0.91	0.90
20.	Quinol	0 00	0 76	0.80	1 00	0.00	0 90	0.81
21.	Picric acid	0 73	0 60	0.56	0.60	0 57	0.60	0.81
22	Vanilline	0 00	0 59	0.59	0.54	0 05	0.80	0 83
23.	Thymol blue	0 82	0 00	0.00	0 00	0.00	1 00	0 95
24	1,2,5,8-Anthroxy anthraquinone	0.00	0 00	0 00	0 00	0.00	0 00	0.00
25.	4-(4-Nitrophenyl)-azo resorcinol	0 18	0.09	0.09	0 09	0.09	0 61	0 68
26.	Di-(2-hydroxyphenylimino) ethane	0 00	0 00	0 00	0 00	0.00	0.61	0.54
27.	8-Hydroxy-7-iodoquinoline-5-sulphonic acid	0 13	0 00	0.00	0 00	0 00	0 56	0.54
28	Phenylfluorone (9-phenyl-2,3,7-trihydroxy-6-fluorone)	0 00	0 00	0 00	0 00	0 00	0.00	0.00
29	Trihydroxy-6-fluorone	0 00	0.00	0.00	0 00	0 27	0 00	0.00
30	4-Chlorophenol	0 54	0 50	0 54	0 81	0.62	0.91	1.00
31.	Bromocresol green	0.82	0 67	0 86	0 68	0 59	0.65	0.81

The detection of phenols using ferric hydroxide impregnated papers can be made without the use of a separate detecting reagent for chromatographic studies.

Chromatography : 31 phenols were chromatographed in aqueous solution of sodium nitrate (1.0 *M*, 0.1 *M*, 0.01 *M*), water, alcohol, water + alcohol (1 : 1) and NaCl (1 0 *M*). The R_f values in different solvent systems are presented in Table 1.

The important separations of phenols were achieved on the basis of difference in R_f values in different solvent systems, e.g. α-naphthol from β-naphthol, 2,4-dinitrophenol from *o*-nitrophenol, 4-chlorophenol from phenol, picric acid from 2, 4-dinitrophenol, catechol from quinol, pyrogallol from resorcinol, 1-nitroso-2-naphthol from α-naphthol, 4-(4-nitrophenyl)-azo resorcinol from resorcinol in 0 1 *M* $NaNO_3$; *m*-cresol from α-naphthol in 0.01 *M* $NaNO_3$; phloroglucinol from pyrogallol in 1.0 *M* NaCl ; and *o*-nitrophenol from *p*-nitrophenol in alcohol solvent system as binary separations, and picric acid from 2,4-dinitrophenol and catechol, α-naphthol from β-naphthol and resorcinol, *o*-nitrophenol from picric acid and 2,4-dinitrophenol and bromocresol from vanilline and di-(2-hydroxyphenylimino) ethane as ternary separations in 0.1 *M* $NaNO_3$ solvent system.

The time required for the ascend of the solvent to a height of 11 cm was approximately 30 min. This shows the importance of the ferric hydroxide papers using simple aqueous systems and thus achieving clean separations in a short period. The use of ferric hydroxide increases the compactness of the spots and removes the tailings, which are commonly observed with plain papers in these simple solvent systems. Ferric hydroxide[3] being a weak inorganic ion exchanger shows a selectivity towards the various phenols which are weakly ionized. This fact gives the basis for separations.

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Studies on 3-Oxo-Glutaric Acid Dianilide. Part—I : Acid-Base Properties

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THE fact that several di- and tri-keto compounds (their enol forms) have wide application in analytical chemistry has created renewed interest in their analytical properties such as acid-base properties, and behaviour as metallochromic indicators with the emphasis on specificity or selectivity, stoichiometry and sensitivity.

A number of these compounds[1,2] have been thoroughly investigated, their absorption spectra recorded and the stability constants and composition of some of their metal complexes established. The acid-base properties and keto-enol equilibria of some β-di- and tri-keto compounds were studied by several investigatiors, using pH-metric[3,4], spectrophotometric[5,6], nmr[7,8] and polarographic[9,10] methods.

The present work aims to throw light on the phenomena and processes taking place as the acidity of acetone dicarboxylic acid dianilide and its chloride and methyl derivatives [ADDA (I), p-Cl-ADDA (II) and p-CH_3-ADDA (III), respectively] is changed, depending on the substituted group. In order to investigate the acid-base properties of compounds I, II and III, titrations of their dilute solutions against standard sodium hydroxide solution were carried out potentiometrically. From the plot of log [salt]/[acid] vs pH (Fig. 1), the pK values of the hydroxyl groups of the enol forms were determined. The absorption spectra of compounds I, II and III were studied in the uv region at various pH values to determine the ionization constants of their weaker hydroxyl groups and to confirm the pH-measurements.

Experimental

Reagents and equipments : All reagents used were of A. R. grade.

Dianilides (I, II, III) : The tri-ketoanilides under investigation were prepared by heating ethyl acetone dicarboxylate (1 mole) with amine (2 moles) in 30 ml pyridine for 4 hr. The crude products were crystallized twice from ethanol in 80% yield[11]. The 10^{-3} M solutions of dianilides (I, II, III) were prepared by dissolving the required amount of these compounds in known volumes of ethanol and dilute solutions were prepared by appropriate dilution, using the same solvent. Ethanol-water
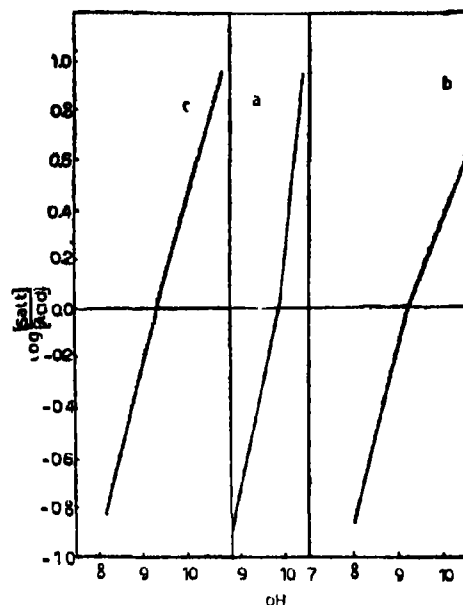
Fig. 1 (*a*) p-CH_3-ADDA , (*b*) p-Cl-ADDA ; (*c*) ADDA.

(1 : 1) solutions were used for studying the absorption spectra.

A Beckman pH-meter H-2 model G 8509 with T-2 titration attachment was used for recording the pH and a PYE Unicam UV spectrophotometer, Model 1750, with 1 cm quartz cells was used for recording the absorbance at different pH values. The titration cell consisted of a 100 ml beaker, a microburette and calomel electrodes. 0.01 M solution of NaOH (carbonate free) was used for titration and 0.01 N solution of Na_2CO_3 and 0.01 N solution of HCl were used for adjusting the pH. The water used was twice distilled from all glass equipments.

pH-*metric titration :* 5 ml of 0.01 M solution of ADDA or one of its two derivatives, p-Cl-ADDA and p-CH_3-ADDA, was taken in the titration cell and 50 ml of alcohol-water mixture (1 : 1) was added. The mixed solution was titrated with 0.01 M sodium hydroxide solution, keeping the tip of the burette immersed in the solution. The pH of the solution was recorded after each addition of alkali.

Absorbance measurements : 8×10^{-5} M solutions of ADDA or p-Cl-ADDA and 5×10^{-5} M solution of p-CH_3-ADDA were prepared by dilution of the respective stock and 10 ml portion of each was taken, pH adjusted to the required value with Na_2CO_3 or HCl solution and absorbances in the region 210 to 350 nm were recorded. Alcohol-water mixture (1 : 1) was used as blank. pH of the solutions were also checked immediately after each set of measurements.

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Results and Discussion

The results obtained in the titration of 5 ml 10^{-3} *M* ADDA (I), *p*-Cl-ADDA (II) or *p*-CH_3-ADDA (III) against 0.01 *M* NaOH indicate that the extent of ionization increases in the order of *p*-CH_3-ADDA, ADDA, *p*-Cl-ADDA. The calculated *p*K values, at the intersection of the straight line of the plot of log [salt]/[acid] vs *p*H (Fig. 1 a, b and c), amount to 9.90, 9.35, 9.25.

A typical absorption spectrum of the compound (III) (Fig. 2) in solutions of different *p*H values from 1.4 to 7.0 is characterized by a sharp band at 250 nm which is due to a π-π^* transition within the conjugate system of the molecules (i, ii, iii), as given by the equilibria,

R or X–C_6H_4–NH–C(=O)–CH_2–C(=O)–CH_2–C(=O)–NH–C_6H_4–X or R

(Ia)

⇌

R or X–C_6H_4–NH–C(O···H–O)=CH–C=CH–C(O–H)–NH–C_6H_4–X or R

(Ib)

⇌

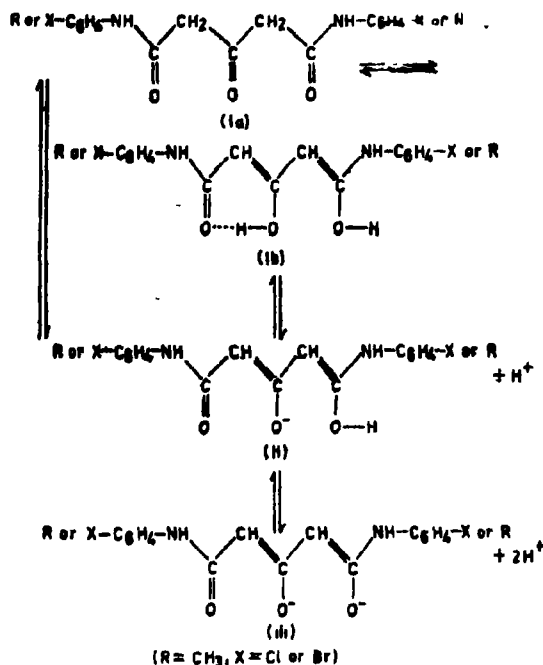
R or X–C_6H_4–NH–C(=O)–CH=C(O^-)–CH=C(O–H)–NH–C_6H_4–X or R $+ H^+$

(ii)

⇌

R or X–C_6H_4–NH–C(=O)–CH=C(O^-)–CH=C(O^-)–NH–C_6H_4–X or R $+ 2H^+$

(iii)

(R = CH_3, X = Cl or Br)

The fact that the absorption spectra is unchanged over the *p*H range 1.4 to 7.0 confirms high *p*K values of the enol form (i). The increase of *p*H from 7.0 to 12.0 results in a hypochromic effect and a subsequent decrease in E from 28400 to 19000 for the primary band at 250 nm. Ascending band appears at 300 nm in case of I and III and at 310 nm in case of II. The intensity of this band increases with the increase of *p*H reaching the limiting value with E of 20500 at *p*H 12, which may be assigned to the π-π^* transition of the forms (ii and iii).

The first decrease in absorbance at 250 nm is attributed to the ionization of OH of the enol forms (i and ii) of the anilide carbonyl groups. This is substantiated by the fact that the ionization of the OH groups which are not involved in a hydrogen bond, requires a lower energy[12]. Also the tautomerism favouring the participation of the anilide carbonyl in hydrogen bonding in structure (i) may retard the ionization of the OH of the enol form of the acetone carbonyl which is confirmed by increase in absorbance at 300-310 nm within the *p*H range 7-12. These results are in good agreement with these obtained by *p*H measurements.

The presence of some isobestic points in the absorption spectra is an indication of the equilibria, existing previously (i, ii and iii).

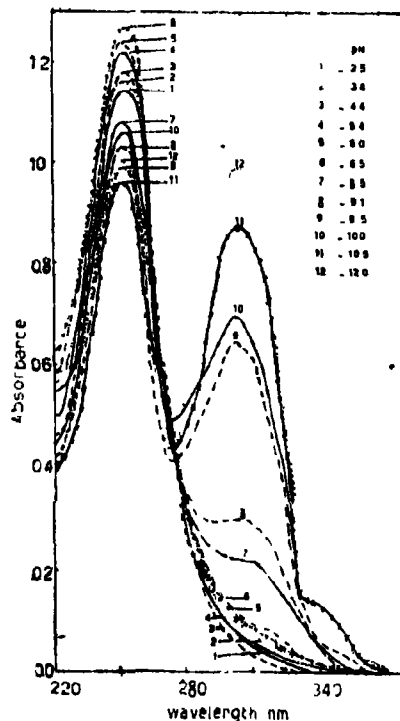



Fig 2 Absorption spectra of 5×10^{-5} *M* *p*-CH_3-ADDA in solutions of varying *p*H values.

The variation of absorbance with *p*H is used for calculating *p*K values using recommended procedure[13]. These values differed within ± 0.1 from the *p*H-metric data. Therefore, both *p*H-metric and spectrophotometric data indicate that *p*-Cl helps and *p*-CH_3 decreases the ionization of the parent ADDA. This becomes more clear by the calculation of the standard free energy changes from the ionization constants of the given compounds (Table 1).

TABLE 1

Compound	X or R	*p*K	ΔG° Kcal mol^{-1}
I	H	9.35	12.838
II	Cl	9.25	12.696
III	CH_3	9.90	13.588

The difference between ΔG° of *p*-Cl-ADDA and that of ADDA is equal to −0.137 Kcal mol^{-1} and means that Cl helps ionization of enol form of *p*-Cl-ADDA, whereas the difference between free

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Study of Transition and Non-Transition Metal Complexes with 3-Amino-2-Benzoylbenzofuran

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The complexes of 3-amino-2-benzoylbenzofuran, (L), with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been synthesized and characterised on the basis of chemical analysis, conductance, magnetic measurements, electronic and infrared spectral studies. Co(II), Zn(II), Cd(II) and Hg(II) complexes are found to possess tetrahedral structure whereas Ni(II) and Cu(II) complexes exhibit polymeric, octahedral structures and Cu(II) complex undergoes Jahn-Teller distortion.

BENZOFURAN derivatives are well known as biologically and pharmacologically important compounds[1-8]. There are reports on metal complexes of benzofurans and their derivatives[4-7], but no information on metal complexes derived from 3-amino-2-benzoylbenzofuran is available. The present communication is a part of a programme to study such complexes and deals with the synthesis and structural features of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of 3-amino-2-benzoylbenzofuran.

Experimental

Materials : The chemicals used in this investigation were of analytical grade.

Ligand : 3-Amino-2-benzoylbenzofuran was prepared by the known[8] procedure.

Preparation of the complexes : Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) complexes were prepared by treating the hot ethanolic solution of the ligand with ethanolic solution of corresponding metal chloride in 1 : 1 molar ratio. The reaction mixture was refluxed for about 1-2 hr. The solution was then reduced to a smaller volume on water bath, cooled and treated with petroleum ether (60-80°) to isolate the respective metal complexes, except Cu(II) complex, for which the solution was concentrated to a pasty mass and treated with solvent ether in excess. The respective solid complexes were filtered and dried over anhydrous $CaCl_2$ in a desiccator.

Cd(II) complex : Ethanolic solutions of the metal chloride ($CdCl_2.2.5H_2O$) and the ligand, in molar ratio 1 : 1, were mixed with vigorous stirring. The resulting mixture was refluxed for 2 hr. The precipitation of the complex was aided by further digestion on water-bath for about 1 hr. The resulting precipitate was filtered, washed with hot ethanol and dried in a desiccator over anhydrous $CaCl_2$.

All the complexes were further purified by Soxhlet.

Chemical analysis : The complexes were analysed for metal and halogen by standard methods. Nitrogen was estimated by Kjeldahl method[9].

Physical measurements : The molar conductance of the complexes were measured, using ELICO CM-82 conductivity bridge with a cell having cell constant of 1.0 cm^{-1}. The magnetic susceptibility measurements were made on a Gouy balance at room temperature, using $Hg[Co(SCN)_4]$ as calibrant. The ir spectra of the ligand and the complexes in nujol mull were recorded on Perkin-Elmer 297, in 4000-600 cm^{-1} region. The far ir spectra of the complexes in nujol mull were recorded on Perkin-Elmer 599 spectrophotometer using CsI plates. The electronic spectra were recorded on ELICO model CL-24 spectrophotometer in 900-340 nm region in DMF.

Results and Discussion

All the complexes are soluble in common organic solvents. except Ni(II) and Cu(II) complexes which are soluble in DMF and DMSO. The molar conductance of all the complexes, except Ni(II) and Cu(II) complexes, in DMF (10^{-3} *M*) fall in the range of 1-12 ohm^{-1} cm^2 $mole^{-1}$, indicating that they are non-electrolytes[10].

In the case of Ni(II) and Cu(II) complexes, the observed conductivity values (Table 1) in DMF (10^{-3} *M*) indicate the complexes to be 1 : 1 electrolytes[11].

Magnetic moment : The magnetic moments of Co(II), Ni(II) and Cu(II) complexes calculated from the corrected magnetic susceptibilities (at room temperature) are given in Table 1. The observed magnetic moment, 4.9 B.M., of the Co(II) complex is higher than the 'spin only' value of three unpaired electrons and is considered to be due to large orbital contribution in a tetrahedral environment. The magnetic moment, 3.1 B.M., observed for the Ni(II) complex is within the range of 2.9-3.4 B.M. reported[12] for octahedral complex.

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TABLE 1—ANALYTICAL DATA, MAGNETIC SUSCEPTIBILITY AND CONDUCTANCE FOR Co(II), Ni(II), Cu(II), Zn(II), Cd(II) AND Hg(II) COMPLEXES

Complex	Metal% Found (Calcd)	N% Found (Calcd)	Cl % Found (Calcd)	μ_{eff} B.M	Molecular conductivity $ohm^{-1}cm^2 mole^{-1}$
$CoLCl_2$	15 98 (16.06)	3 85 (3.81)	18.97 (19.85)	4.9	3 45
$NiLCl_2.H_2O$	14 92 (15 26)	3.53 (3.64)	18 65 (18.46)	3.1	66 51
$CuLCl_2$	17.41 (17.1)	3.68 (3 77)	19.29 (19.11)	1.9	90.01
$ZnLCl_2$	17 29 (17.51)	3.46 (3.74)	18.83 (19 01)	—	12.01
$CdLCl_2 H_2O$	25.78 (25.64)	3.32 (3 19)	16 29 (16.19)	—	1 42
$HgLCl_2$	39 72 (39.43)	3.05 (2 75)	13.73 (13.9[illegible])	—	3 32

The magnetic moment value of the Cu(II) complex lies within the range of 1.67-1.90 B.M., which indicates that the complex does not involve spin-spin interaction. However, the polymeric nature of the complex cannot be precluded, as the polymeric complexes with no spin interaction are known in literature[13,14]. Zn(II), Cd(II) and Hg(II) being d^{10} ions show diamagnetism.

Electronic spectra : The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes are characterised by the band maxima around 660 nm with a shoulder at 590 nm, 725 nm – 675 nm, and 690 nm, respectively. All these complexes display an absorption peak centered around 410 nm. Considering the intensity of this band, we have attributed it to the L→M charge transfer band.

It is known[15] that Co(II) complex in tetrahedral environment exhibits a high intensity multiplet (600-700 nm) due to $^4A_2 \rightarrow {}^4T_1(P)$ transition. The observed band maxima lie very well in the region of tetrahedral configuration. The Ni(II) complex exhibits a spectrum typical of octahedral environment. It is documented in literature[16] that d^8 system, viz. Ni(II), displays three bands in the 400-1400 nm region. These have been attributed to various transitions. The limit of our spectrophotometer does not allow the location of the band due to $^3A_{2g} \rightarrow {}^3T_{2g}$ transition. However, the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition for the complex under consideration occurs in the region 725-675 nm as a split band. The splitting envisaged in the transition may be due to the spin-orbital coupling. The transition due to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ has been overlayed by the high intensity charge transfer band around 410 nm. It is evident from literature[15] that the Cu(II) complexes in an octahedral environment show a broad band around 800 nm due to $^2E_g \rightarrow {}^2T_{2g}$. This is highly sensitive to Jahn-Teller distortion and shifts hypsochromically with an increase in the tetragonal distortion. The observed band in the region 680 nm can be considered to be due to $^2E_g \rightarrow {}^2T_{2g}$ and the hypsochromic shift indicates the distortion brought about in the complex due to Jahn-Teller phenomenon.

Zn(II), Cd(II) and Hg(II) being d^{10} ions do not show d – d transitions Therefore, the stereochemistry of their complexes cannot be derived from their electronic spectra. The information on their structure has, therefore, been derived from ir spectral measurements only.

Infrared spectra : Selected infrared frequencies along with their tentative assignments are listed in Table 2. In the ir spectra of Ni(II) and Cd(II) complexes, broad band around 3500-3450 cm^{-1} due to ν(OH) of water molecule appears. On heating the complexes above 110°, the water molecule is lost showing that it is lattice held and not coordinated. The bands observed in the region 3400-3100 cm^{-1} are attributed to the ν(NH) vibrations. The coordination of the metal through nitrogen should cause splitting of these bands and decrease in their intensities[16], or shifting of these bands towards low frequency side. The Co(II), Cu(II), Cd(II) and Zn(II) complexes of 3-amino-2-benzoylbenzofuran show neither such splitting nor shifting towards low frequency side, indicating non-involvement of NH_2 group in bond formation. In the case of the Ni(II) and Hg(II) complexes, ν(NH) band shifts towards low frequency side, indicating the involvement of NH_2 group in bond formation.

In the case of 3-amino-2-benzoylbenzofuran complexes, the ligand band observed at 1625 cm^{-1}

TABLE 2—SELECTED INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF THE LIGAND AND ITS METAL COMPLEXES

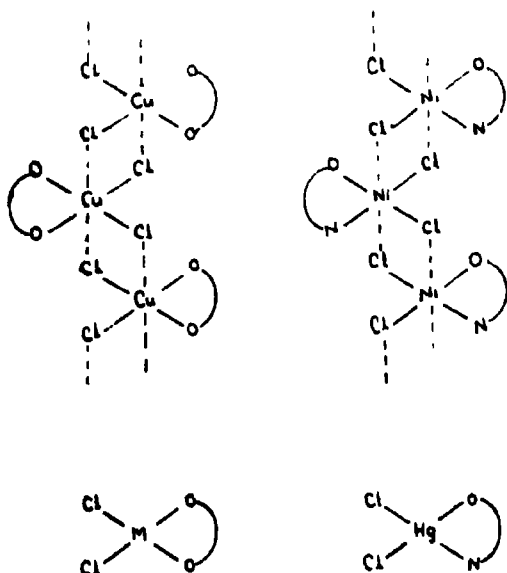
Ligand (L)	$CoLCl_2$	$NiLCl_2.H_2O$	$CuLCl_2$	$ZnLCl_2$	$CdLCl_2 H_2O$	$HgLCl_2$	Assignment
—	—	3500-3450b	—	—	3500-3450b	—	ν(OH)
3418mb	3520b	3400w	3430m	3430w	3440s	3380ms	
3280mb	3380b	3280w	3320b	3320w	3330s	3270ms	ν(N – H)
3170mb	—	3160w	—	3180b	3170w	3160w	
1625s	1610ms	1620ms	1590mb	1615ms	1620s	1610ms	ν(C = O)
1250w	1245w	1250w	1245vw	1240w	1250w	1250w	
1170mb	1165mb	1170b	1145b	1175s	1180s	1175ms	ν(C – O – C)
—	—	—	—	1150sh	1165sh		
—	490m	—	505ms	490m	500ms	—	ν(M – O) furan ring oxygen
—	300w	320w	300s	290w	262w	325w	ν(M – O)
—	—	235ms	—	—	—	420s	ν(M – N)
—	330w	—	—	280w	220w	290s	ν(M – Cl)
—	—	282w	280w	—	—	—	$\nu(M - Cl)_b$

s = strong, w = weak, m = medium, ms = medium strong, mb = medium broad, vw = very weak, b = bridging, sh = shoulder.

due to ν(C=O) has been shifted towards lower frequency side in all the complexes. This shift is suggestive of coordination of (C=O) group through oxygen[17].

The ligand band observed in the range 1075-1250 cm^{-1} has been attributed to the ν(C-O-C) mode in view of previous assignments[18,19]. This band shifts towards the lower frequency side in the case of Co(II), Cu(II), Cd(II) and Zn(II) complexes indicating the involvement of furan ring oxygen in bond formation, whereas in the case of the Ni(II) and Hg(II) complexes no such shift is observed indicating non-involvement of furan ring oxygen in bond formation. In the complexes of Co(II), Cu(II), Cd(II) and Zn(II), a very sharp band observed at 500±10 cm^{-1} is the band involving the metal and furan oxygen linkage[20,21].

The low frequency bands in the range 325-260 cm^{-1}, not observed in the ligand spectrum, are assigned to M-O stretching vibration in all the complexes and agree well with previous assignments[22,23]. The bands observed at 420 cm^{-1} and 235 cm^{-1} in the spectra of Ni(II) and Hg(II) complexes respectively, have been assigned to ν(M-N) vibrations[23]. The bands in the range of 330-220 cm^{-1} are assigned to ν(M-Cl) vibrations[23-25] in all the complexes except Ni(II) and Cu(II) complexes. In the case of Ni(II) and Cu(II) complexes, which exhibit polymeric nature, a band around 280 cm^{-1} is assigned to the ν(M-Cl)$_b$ which agrees well with previous assignments[23].

In view of the spectral observations taken together with analytical data, magnetic moments and molar conductance, we propose the following structures for the complexes.

M=Co(II), Zn(II) and Cd(II)

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Alkaline Earth Metal Complexes : Mixed Ligand Complexes of Some Organic Compounds of Magnesium with Nitrogen Donor Ligands

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Mixed ligand complexes of magnesium salts of salicylic acid, salicylaldehyde, 1-nitroso-2-naphthol, 8-hydroxyquinoline, *o*-nitrophenol and 2-hydroxy-3-naphthoic acid with nitrogen donor ligands 1,10-phenanthroline and ethylenediamine have been synthesised in absolute ethanol. A study of the far infrared region (between 604-470 cm^{-1}) is very conclusive for a *trans* structure for the magnesium complexes formed with ethylenediamine.

COMPARED to those of transition and rare-earth metals, mixed ligand complexes of magnesium with bidentate ligands are less well documented ; only complexes with monodentate ligands have been reported[1,2]. Fenton[3] synthesised a few mixed complexes of magnesium salts with bidentate ligands, viz., ethylenediamine, *o*-phenanthroline, 2,2'-bipyridyl, etc. We have extended the investigation by synthesising some new mixed ligand complexes of magnesium metal salts of salicylic acid (SalA), salicylaldehyde (SalH), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), *o*-nitrophenol (ONP) and 2-hydroxy-3-naphthoic acid (2H3NA) with nitrogen donor ligands 1,10-phenanthroline and ethylenediamine.

Experimental

For the different organic acid salts of magnesium, our usual method of synthesis was to take a suspension of magnesium hydroxide in absolute ethanol and to add to it the above mentioned ligands, (having replaceable protons HL'), in slight excess. The reaction was allowed to take place for 5 to 6 hr on a hot plate magnetic stirrer when magnesium hydroxide, which is insoluble in absolute ethanol, passed into solution. Coloured compounds separated out on cooling, which were filtered, washed with absolute ethanol and dried at 90°.

To the suspension of these organic acid salts of magnesium in absolute ethanol, a saturated solution of 1,10-phenanthroline or ethylenediamine was added drop by drop in slight excess, with constant stirring. After 3 to 4 hr, the suspended salts passed into solution, which were then concentrated. On cooling, adducts of the general formula MgL_2.en/phen, (where L = organic acids), separated out which were filtered, washed with absolute ethanol and dried in an oven at 90°. The number of ethylenediamine/phenanthroline molecules attached was always found to be one.

The colour, transition or decomposition temperatures and analytical values of the compounds are given in Table 1.

Results and Discussion

Different organic acid salts of magnesium : All these compounds are stable under dry condition. When exposed to atmosphere they absorb 2 molecules of water.

The infrared spectra of $Mg(SalA)_2.2H_2O$ complex indicate that O – H is strongly hydrogen bonded. The O - H stretching band of SalA at 3240 cm^{-1} shows up as a broad peak between 3200-3040 cm^{-1}. Further, there are two humps at 2700 and 2600 cm^{-1}. The antisymmetric stretching frequency at 1660 cm^{-1} of the COO^- group in salicylic acid is shifted down to 1630 cm^{-1}.

In the compound with salicylaldehyde, the C=O frequency at 1630 cm^{-1} is much lower than that observed for free salicylaldehyde (1700 cm^{-1}).

In magnesium-*o*-nitrophenolate, the antisymmetric (1510 cm^{-1}) and symmetric (1335 cm^{-1}) stretching frequency of the nitro group of ONP is shifted to 1520 cm^{-1} and 1315 cm^{-1}, respectively, suggesting association of the NO_2 group in the magnesium compound.

There is a broad absorption at 3300-3000 cm^{-1} with a hump at 3040 cm^{-1} in the 2-hydroxy-3-naphthoic compound. Moreover, there is another broad peak at 2700 cm^{-1}, which indicates that there is strong hydrogen bonding in the compound. The C=O peak at 1 59 cm^{-1} of the acid is observed at 1620 cm^{-1} in the magnesium compound.

Complexes formed with the above salts : The complexes formed by these different organic acid salts of magnesium with 1,10-phenanthroline or ethylenediamine are stable when stored dry. The transition or decomposition temperatures of these adducts are much higher than the melting/boiling

TABLE 1

Compound	Colour	Transition (t°C) or decomp. (d°C) temp.	Calcd.(%)				Found(%)			
			C	H	N	M	C	H	N	M
$Mg(SalA)_2.2H_2O$	White	298d	52.14	4 34		7.45	51 78	4.19		7 16
$Mg(SalA)_2$.phen	White	285d	65.27	3.76	5.85	5.02	64 82	3.52	5.53	4.86
$Mg(SalA)_2$ en	Dirty white	172t & 240d	53.68	5.02	7.82	6.40	52.95	4.74	7.43	6.32
$Mg(SalH)_2$	Pale yellow	315d	63.15	3.75		9.02	62 76	3,48		8 76
$Mg(SalH)_2$ phen	Pale yellow	240d	69.95	4 08	6 29	5 38	69 43	3.86	5.86	5 02
$Mg(SalH)_2$.en	Yellow	168t	58.89	5.52	8.58	7.36	58.27	5 28	7.97	6.83
$Mg(1N2N)_2$	Green	300d	65.21	3.26	7.60	6.52	64.68	3 09	7 31	6.15
$Mg(1N2N)_2$.phen	Light green	250d	70.07	3.64	10 21	4.37	69.87	3.62	9.26	3 79
$Mg(1N2N)_2$.en	Brownish green	166t	61.68	4.67	13.08	5.60	60.79	4.18	12.54	5.12
$Mg(ONP)_2$	Orange	180d	48.00	2.66	9.33	8.00	47 64	2.41	8.92	7.64
$Mg(ONP)_2$.phen	Orange	160t	60 00	3.33	11.66	5 00	59 62	3 12	11.28	4.86
$Mg(2H3NA)_2.2H_2O$	Dirty white	295d	60.82	4.14		5 53	60 13	3.92		5.37
$Mg(2H3NA)_2$.phen	White	252d	70.58	3.80	4.84	4.15	69.87	3.62	4.26	3.79
$Mg(2H3NA)_2$ en	Light green	162t	62 88	4.80	6 11	5 24	62.24	4.42	5.67	4.92
$Mg(8HQ)_2$.phen	Yellow	240d	73.17	4.06	11.38	4.87	72.48	3 91	10.73	4.32
$Mg(8HQ)_2$ en	Pale yellow	150t	64.51	5.37	15.05	6.45	63.65	5.00	14.82	6.21

points of the corresponding ligands showing the greater stability. That these adducts are genuine complexes and not stoichiometric mixtures, is clear from the fact that organic salts of magnesium, which remain in suspension in absolute ethanol, passes into solution on addition of the second ligand i.e. 1,10-phen or en and the adducts then separate out from the above ethanolic solution.

In all the magnesium complexes formed with 1,10-phenanthroline, the corresponding *phen* absorptions are there, but none have been found to be metal sensitive.

The blue shift in the NH_2 stretching vibrations in the 3340 to 3250 cm^{-1} region clearly shows that *en* is coordinated to the metal. As regards conformation of *en* in these complexes, multiplicity of certain infrared bands have been used as the criteria.

One broad band is observed at 1600 cm^{-1} region in all these complexes; only $Mg(2H3NA)_2$.*en* shows two at 1605 and 1624 cm^{-1}. The $Mg(SalH)_2$.en and $Mg(1N2N)_2$.en show only one band at 1100 cm^{-1} and 1132 cm^{-1}, respectively, whereas $Mg(SalA)_2$.en has two in that region at 1090 and 1135 cm^{-1}. The *cis*-complex usually shows four bands in that region.

Moreover, the bands observed in far infrared region (between 604-4˜0 cm^{-1}) are very conclusive for a *trans* structure (Table 2) for all these magnesium

TABLE 2—SELECTED NH_2 BANDS (cm^{-1}) IN THE FAR INFRARED REGION

$Mg(SalA)_2$.en	470	500	515
$Mg(SalH)_2$ en	520	535	555
$Mg(1N2N)_2$ en	515	530	560
$Mg(2H3NA)_2$.en	510	542	552

complexes. In conformity with the observations that *trans* complexes of *en* show three bands between 604-470 cm^{-1}, all these magnesium complexes have three bands in that region. Further, the pattern of distribution of the bands is also even in that region. For a *cis*-isomer, one expects four or more in that region and the pattern is three (or more) clustered together, and one farther removed. As such, a *trans-en* polymeric structure can be suggested for all these complexes.

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Mixed Ligand Anionic Complexes of Cadmium(II)

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Sixteen mixed ligand anionic complexes of cadmium(II) having the composition $[M]_2[CdCl_4L_2]$, $[M]_2[CdCl_4L']$, $[M]_2[CdCl_4L'']$ and $[M][CdCl_3L''']$, where M = monomethylammonium cation, L = pyridine, β-picoline, γ-picoline, quinoline, 4-aminopyridine, piperidine or thiourea ; L' = α-picoline, quinaldine or 2,6-lutidine ; L'' = ethylenediamine, o phenylenediamine, 1-10-phenanthroline or 2-2'-bipyridine ; L''' = oxine or piperidyldithiocarbamate, have been synthesized. The compounds of the first and third categories are octahedral and the later two types are penta-coordinated as inferred from elemental analysis, conductance and ir spectral studies.

DIVALENT cadmium forms several four coordinated tetrahedral complexes[1,2] with a variety of ligands containing O, N, S potential donor sites, involving the use of 5S 5P^3 hybrid orbitals. Even though the complexes of the composition CdX_3^- and CdX_4^{2-}, where X = Cl$^-$ and SCN$^-$, have been studied[3] in detail potentiometrically, little work has been done to change the stereochemistry of these anionic complexes by reacting with other nitrogen and sulphur donor ligands. To increase the coordination number, particularly to synthesize complexes of coordination number five, we had earlier reported[4,5] penta-coordinated base-adducts of Zn(II) and Cd(II) dithiocarbamates with N and S donor ligands Some anionic mixed ligand complexes of Co(II) and Ni(II) exhibiting unusual coordination number have also been reported[6,7]. This communication describes the preparation and characterisation of sixteen anionic mixed ligand complexes of cadmium(II) containing monomethylammonium chloride and nitrogen and sulphur donor ligands.

Experimental

All chemicals used were of A. R. grade. An ethanolic solution of cadmium(II) chloride was treated with an ethanolic solution of monomethylammonium chloride in 1 : 2 ratio when a white crystalline compound separated out immediately. This was filtered, washed with ethanol and dried *in vacuo*.

The mixed ligand complexes were prepared by adding requisite amount (1 . 2 ratio) of the nitrogen/sulphur donor ligands to the methanolic solution of di-monomethylammonium tetrachlorocadmium(II). In some cases the compounds were formed immediately and in some cases refluxing was continued for 2 to 3 hr till a clear solution was obtained. A shining needle-shaped crystalline compound separated out on cooling, which was washed with ethanol, followed by ether and dried *in vacuo*.

Cadmium, nitrogen and chloride were estimated by following the standard methods. The conductance measurements were carried out at room temperature with 10^{-3} *M* solution in acetone medium using a Toshniwal conductivity bridge. IR spectra of the complexes were recorded on KBr phase using Beckman IR-20 spectrophotometer. Relevant analytical and conductance data are given in Table 1.

Results and Discussion

Analysis and conductance data indicate that the complexes have the following composition : $[M]_2$-$[CdCl_4L_2]$, $[M]_2[CdCl_4L']$, $[M]_2[CdCl_4L'']$ and $[M][CdCl_3L''']$, where M = monomethylammonium cation ; L = pyridine, β-picoline, γ-picoline, quinoline, 4-aminopyridine, piperidine or thiourea, L' = α-picoline, quinaldine or 2,6-lutidine ; L'' = ethylenediamine, o-phenylenediamine, 1-10-phenanthroline or 2-2'-bipyridine and L''' = oxine or piperidyldithiocarbamate.

All the compounds have high melting points and are white, greyish-white to yellow in colour, soluble in acetone in which medium the Λ_M values are around 230 mhos cm^2 indicating 2 : 1 electrolytic nature of the first fourteen complexes. The Λ_M values for the last two complexes are ~115 mhos cm^2 indicating them to be 1 : 1 electrolytes.

Study of ir spectra is quite informative. Absorption bands are noticed at 930(vs), 980(s), 1260(vs), 1410(s), 1485(s) and 3150(s) cm^{-1}, characteristic of the bands due to monomethylammonium chloride, modified due to complexation. Most of the absorption bands due to free sulphur and nitrogen donor ligands have been modified in the anionic mixed ligand complexes, indicating their bonding to the cadmium(II) ion. In sodium salt of piperidyldithiocarbamate, the appearance of bands at 840 and 1260 cm^{-1} can be assigned to thiol (C–S) and thiocarbonyl (C=S) absorption bands, respectively. In Cd(II) complexes, shifting of these bands to lower

TABLE 1—ANALYSIS, MELTING POINT AND CONDUCTANCE DATA

Compound	m.p. °C	%Cd		%N		%Cl		Λ_M mhos cm²
		Found	Reqd	Found	Reqd.	Found	Reqd.	
$[M]_2[CdCl_4(Py)_2]$	>250	23.52	23.69	11.72	11.80	29.47	29.77	240.00
$[M]_2[CdCl_4(\beta\text{-Pic})_2]$	>250	22.17	22.46	11.12	11.19	28.08	28 12	230.00
$[M]_2[CdCl_4(\gamma\text{-Pic})_2]$	>250	22.29	22.46	11.07	11.19	28.02	28 12	245.00
$[M]_2[CdCl_4(4\text{-Ap})_2]$	>250	22.16	22.28	16 67	16.65	27 92	28.01	225.00
$[M]_2[CdCl_4(Q)_2]$	>250	19.32	19.56	9.68	9.74	24 35	24 60	220.00
$[M]_2[CdCl_4(tu)_2]$	>250	33.81	28 91	11 85	11 93	30 06	30.15	215 00
$[M]_2[CdCl_4(Pip)_2]$	250	22 95	23 10	11 43	11 51	28 95	29 04	240 00
$[M]_2[CdCl_4en]$	>250	29.75	29.89	14 72	14 87	32 18	32 35	220.00
$[M]_2[CdCl_4o\text{-Ph.D}]$	>250	26.27	26.48	13.15	13 19	26.48	26 54	230 00
$[M]_2[CdCl_4 1,10\text{-Ph}]$	>250	22 51	22 64	11.16	11 28	28 37	28.46	225 00
$[M]_2[CdCl_4 2,2'\text{Bi}]$	>250	23 62	23 79	11 79	11 85	29 83	29 90	220 00
$[M]_2[CdCl_4(\alpha\text{-Pic})]$	>250	27 35	27 52	10 17	10 28	34.39	34 48	235 00
$[M]_2[CdCl_4(Quin)]$	>250	24 27	24 46	9.08	9.14	30 58	30 74	225 00
$[M]_2[CdCl_4(2,6\text{-Lut})]$	>250	26 43	26 67	9.78	9 96	33 29	33 34	220 00
$[M][CdCl_2(OX)]$	>250	28 48	28 57	7.05	7 11	27 95	28 00	115 00
$[M][CdCl_2(P\text{-dtc})]$	>250	27.32	27 45	6.79	6.83	25 82	25.89	110 00

M = monomethylammonium cation, Py = pyridine, α-Pic = α-picoline, β-Pic = β-picoline, γ-Pic = γ-picoline, Q = quinoline, 4-AP = 4-aminopyridine, tu = thiourea, Pip = piperidine, en = ethylenediamine, o-Ph.D = o-phenylenediamine, 1,10-Ph = 1,10-phenanthroline, 2,2'-Bi = 2,2'-bipyridine, Quin = quinaldine, 2,6-Lut = 2,6-lutidine, OX = oxine, P-dtc = piperidyldithiocarbamate.

frequency region occurs, indicating coordination through both sulphur atoms ν(C–O) and ν(C=N) of oxine appear at 1200 cm^{-1} and 1590 cm^{-1}, respectively, indicating the coordination of oxine moiety to the Cd(II) ion through hydroxyl oxygen and ring nitrogen atom.

From the analysis, conductance and ir spectral studies, the compounds of the first and the third categories are octahedral in configuration. The compounds of the second category are presumed to be penta-coordinated because of the mono-adduct formation favoured by the sterically hindered nitrogen donor ligands like α-picoline, quinaldine and 2,6-lutidine The compounds of the fourth category are also penta-coordinated as inferred from analysis, conductance and ir spectral data. In view of the spherical nature of Cd(II) ion and absence of crystal field effects, this possibility is not entirely unexpected. However, X-ray crystallographic study will reveal the exact stereochemistry of these complexes.

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Isolation, Characterisation and Antimicrobial Activity Studies of the Mixed Ligand Complexes of Cd(II) with 8-Hydroxyquinoline and Various Salicylic Acids

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A series of mixed ligand complexes of Cd(II) with the general formula CdL_1L_2 (where L_1 = 8-hydroxyquinoline ; L_2 = salicylic acid, 5-chloro, 3,5-dibromo, 3,5-diiodo, 3,5-dinitro acetyl salicylic acids) are isolated in pure state and characterised by elemental analysis and infrared data. The low molar conductance of these complexes in DMF indicates non-electrolyte nature of these complexes. The antimicrobial activity of these complexes against 14 pathogenic bacteria and 5 fungi is studied under various conditions. Even though one 8-hydroxyquinoline molecule in the binary cadmium-oxinate is replaced by a low cost fungicide like salicylic acid in the formation of mixed ligand complexes, these mixed ligand complexes are found to posses fairly higher antimicrobial activity against several organisms than the binary cadmium-oxinate. The lypophilic tendency of these complexes is determined and its influence on the antimicrobial activity is critically examined. The probable mechanism of the toxic action of these complexes against various organisms is discussed.

THOUGH 8-hydroxyquinoline (oxine) and its divalent metal chelates are known to possess fungicidal and bactericidal properties, the high cost of 8-hydroxyquinoline limits their applicability. It has been observed by the present authors in the use of oxine chelates as antimicrobial agents that the cost factor can be minimised by replacing one oxine molecule in the divalent metal oxinates of Cu(II)[1], Hg(II)[2] and Cd(II) with a low cost fungicide like salicylic or substituted salicylic acids as heteroligands. A series of mixed ligand complexes of Cd(II) with oxine and salicylic acids are prepared and their antimicrobial activity is studied under various conditions. The relation between their antimicrobial activity and physico-chemical properties is examined critically to understand the mechanism of action. The results of these investigations are presented in this paper.

Experimental

All the chemicals used are of analytical grade (B.D.H.) reagents.

General method for the preparation of the complexes : Equimolar solutions of salicylic acids (0.2 *M*), Cd(II) acetate (0.2 *M*) and 8-hydroxyquinoline (0.2*M*) in 80% aqueous methanol are mixed. After stirring for 0.5 hr, the product is removed by filtration, washed with several volumes of water, digested in acetone and filtered. The complexes are dried at 70° for 12 hr. Metal and nitrogen are estimated by standard methods.

Physical measurements : Infrared spectra are recorded on a Perkin-Elmer model 577 spectrophotometer (4000 cm^{-1} to 200 cm^{-1}) by KBr disc technique. The conductivity of the complexes ($10^{-3}M$) is measured at 27° by Systronics conductivity bridge 305 in dimethyl sulphoxide (DMSO).

Antimicrobial activity : The antimicrobial activity of the compounds in DMSO is examined *in vitro* by serial dilution method[3] against various bacteria and by paper disc method[4] against fungi. All the stock cultures are obtained from the Department of Microbiology, All India Institute of Medical Sciences, New Delhi. Peptone water and saline water are used for making the inoculum for bacteria (18 hr cultures) and fungi, respectively. Nutrient broth and Saborounds dextrose agar (M/s Hindustan Dehydrated Media, Bombay) are used as test media for bacteria and fungi, respectively. The minimum inhibition concentration (MIC ; μg/ml) of the compounds against bacteria and the average zone of inhibition (mm) of the compounds at 1000 μg/ml against fungi are given in the Tables 2 and 3, respectively. All the tests are carried out in duplicate.

Results and Discussion

The elemental analysis of these complexes (Table 1) show that Cd(II) forms mixed ligand complexes of general formula CdL_1L_2 (where L_1 = 8-hydroxyquinoline and L_2 = salicylic or substituted salicylic acids). The low molar conductance

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TABLE 1—ANALYTICAL, CONDUCTOMETRIC AND IR DATA OF THE Cd-OXINE-SALYCILATE MIXED LIGAND COMPLEXES

Sl. No.	Compounds	Colour	Decomp temp. °C	% metal		% nitrogen		Λ mhos cm²	IR frequencies in mixed ligand complexes (cm⁻¹)				
									Oxine			Salicylic acids	
				cal	obs	cal	obs		$\nu(M-O)$	$\nu(C-O)$	$\nu(M-N)$	$\nu_{asy}(O-C-O)$	$\nu_{sy}(O-C-O)$
1.	Cd(OX)(SA)	Greenish yellow	>300	28.55	28.50	3.56	3 52	8.1	380 b	1110 s	500 s	1570 b	1420 s
2.	Cd(OX)(Cl-SA)	Greenish yellow	>300	26 25	26.28	3 27	3 25	8 6	390 b	1110 s	500 s	1570 b	1420 s
3.	Cd(OX)(2Br-SA)	Greenish yellow	>300	20.38	20.36	2.54	2.55	8.4	380 b	1110 s	500 s	1570 s	1420 s
4.	Cd(OX)(2I-SA)	Greenish yellow	292	17 57	17 58	2 18	2.14	8 3	380 b	1110 s	500 s	1570 s	1420 s
5.	Cd(OX)(2NO$_2$-SA)	Golden yellow	298	23.24	23.21	3 69	3.66	8 2	390 b	1110 s	490 s	1570 s	1420 s
6.	Cd(OX)(Ace-SA)	Greenish yellow	>300	25.79	25 81	3 27	3.23	8 4	380 b	1110 s	490 s	1570 s	1420 s

OX = 8-hydroxyquinoline , SA = salicylic acid Cl-SA = 5-chloro salicylic acid , 2Br-SA = 3,5-dibromo salicylic acid , 2NO$_2$-SA = 3,5-dinitro salicylic acid , 2I-SA = 3,5-diiodo salicylic acid , Ace-SA = acetyl salicylic acid , s = sharp , b = broad

TABLE 2—ANTIBACTERIAL ACTIVITY MIC (μg/ml) OF THE CADMIUM COMPLEXES WITH 8-HYDROXYQUINOLINE AND SUBSTITUTED SALICYLIC ACIDS AT 37° AFTER 18 Hr IN NUTRIENT BROTH

Sl No	Compound	Gram-positive		Gram-negative											
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Cd(OX)$_2$	12 5	6 2	12 5	25	50	12 5	50	12 5	100	25	12.5	12 5	12 5	>100
2	Cd(OX)(SA)	6 2	3 1	12 5	100	3 1	50	50	12 5	12 5	25	25	12 5	25	25
3.	Cd(OX)(Cl-SA)	6 2	3 1	12.5	100	3 1	50	100	25	3 1	25	25	12 5	50	50
4	Cd(OX)(2Br-SA)	6 2	3 1	12 5	100	3 1	50	100	12 5	3 1	25	25	12 5	25	50
5.	Cd(OX)(2I-SA)	12 5	6 2	12 5	100	6 2	50	100	25	25	25	25	25	50	50
6	Cd(OX)(2NO$_2$-SA)	6 2	3 1	6 2	100	3 1	50	100	12 5	6 2	25	25	25	50	50
7	Cd(OX)(Ace-SA)	12 5	3 1	25	100	6 2	50	100	25	50	50	25	12.5	25	25

(1) *Staph albus* , (2) *Staph aureus* , (3) *Sch schmitzi* , (4) *Pseudomonas pyocanes* , (5) *Shigella sonnei* , (6) *Klebsilla aerogenes* , (7) *Proteus morganii* , (8) *Shigella flexneri* , (9) *Vibrio cholerae* , (10) *Escherichia coli* , (11) *Salmonella typhi* , (12) *Salmonella paratyphi-A* , (13) *Salmonella paratyphi-B* , (14) *Schigella boydii.*

values of these complexes in DMSO indicate that they are of non-electrolyte type.

Infrared data : The asymmetric $\nu(O-C-O)$ and the symmetric $\nu(O-C-O)$, which appeared in all the salicylic acids around 1600 and 1440 cm^{-1} respectively are found to be shifted in the mixed complexes to lower values of 1570 and 1420 cm^{-1}, indicating metal carboxylate linkage[5,6]. Charles *et al*[7] reported that in several oxine complexes of metals, the $\nu(C-O)$ is observed at 1120 cm^{-1} region but the position of the bands slightly varies with the metal. The $\nu(C-O)$, which appeared in the free oxine molecule at 1090 cm^{-1} is found to be shifted in all the mixed complexes giving a strong absorption band at 1110 cm^{-1} indicating clearly the oxine coordination in the complex. In all the mixed ligand complexes, the observed band in the neighbourhood of 500 cm^{-1} may be identified as M–N stretching frequency[8]. A broad band at 380-400 cm^{-1} in all the complexes may be assigned to metal-oxygen stretching frequency[8].

Antimicrobial activity : The toxic effect of the cadmium-oxine-salicylic or substituted salicylic acid mixed ligand complexes against various bacteria and fungi is found to be either equal or slightly greater than the cadmium-*bis*-8-hydroxyquinoline complex. Salicylic acid or substituted salicylic acids and their cadmium chelates are found to have measurable activity against these bacteria and fungi only at relatively high concentrations (for bacteria >100 μg/ml, fungi >2000 μg/ml). This may be due to their higher water solubility. Albert *et al* explained the antimicrobial activity of copper(II)-*bis*-8-hydroxyquinoline by assuming that this complex first penetrates the cell and undergoes dissociation to a 1 : 1 copper-oxine complex and free oxine at the site of action. The 1 : 1 chelate will become the toxic entity by combining with and blocking metal binding sites on enzymes. Thus the 1 : 2 chelate due to its lipo solubility is necessary to take the toxic moiety i.e. the 1 : 1 charged complex to the site of action. The assumption was supported by the fact that antimicrobial activity of these complexes was reversed in the presence of excess of copper. This may be due to the inability of the ionically charged 1 : 1 chelate (which is produced in the presence of excess of metal) to penetrate the cell membrane. Block[9] proposed that the natural chelates within the cell were poisoned by removing copper from Cu(II)-oxine, thereby freeing oxine which could then bind the metallic prosthetic groups of the enzymes. Zentmyer *et al*[10] proposed a mechanism of detoxication of the 1 : 2 chelate by natural metabolites. The 1 : 2 chelate dissociates to the 1 : 1 chelate, thereby entering the aqueous phase of the cell. Histidine and cystine, which form more

stable complexes with copper than the 1 : 1 chelate of copper and 8-hydroxyquinoline, remove the copper and form lipid soluble chelates. Esposito and Fletcher[11] proposed that the activity of copper(II)-8-hydroxyquinoline was due to the 1 : 1 complex which could bind with an enzyme site involved in the biosynthesis of pteridines. This was based on the reversal of inhibition by several pteridines and precursors. It is also believed that a similar mechanism may be working well in explaining the toxic action of all other bivalent oxinates.

According to Overton's concept of cell permeability, the lipoid membrane surrounding the cell favours the passage of lipid soluble materials through the membrane and lipo solubility is considered as one of the important factors that control the antimicrobial activity of any toxic agent. The partition of the toxic agent between olyl alcohol or chloroform and pH 7.4 phosphate buffer system is considered as a good model to understand the lipophilic or lipophobic tendency[12]. So we have determined the distribution of all these complexes between chloroform and pH 7.4 buffer and the results are given in Table 4. As expected, the cadmium-oxine salicylic acid or substituted salicylic acids mixed complexes have lower partition coefficient in chloroform when compared to cadmium(II)-oxine complex. However, they have equal or slightly more toxic effect against various bacteria and fungi in comparison to cadmium(II)-*bis*-8-hydroxyquinoline complex. This indicates that in the mixed complexes not only the 1 : 1 cadmium oxine complex is having toxic activity but also the released salicylic acid may be playing an important role in the antimicrobial activity through a different mechanism. The salicylic acids or cadmium salicylate chelates, though possessing toxic effects due to their higher water solubility, cannot go to the site of action as much as the mixed complexes can penetrate. If in the mixed complexes also the 1 : 1 cadmium oxine is the only toxic moiety then the antimicrobial activity of the mixed complexes should increase with increasing pK_1 values of the salicylic acids and cadmium-oxine-diiodosalicylic acid must have maximum activity. But no such relation is found to exist from their antimicrobial activity screening studies (Tables 2 and 3) which indicate that salicylic acids also play an important role in the toxic action. It is also believed that if the geometry and charge distribution around the molecule are incompatible with geometry and charge distribution around the peripheries of the pores of the fungal or bacterial cell wall, penetration through the wall by the toxic agent cannot take place and toxic reactions within the spore do not occur. This may be the one of the reasons for certain mixed ligand complexes showing less effective antimicrobial activity than the corresponding $Cd(OX)_2$ complex.

TABLE 3—ANTIFUNGAL ACTIVITY OF THE CADMIUM COMPLEXES WITH 8-HYDROXYQUINOLINE AND SALICYLIC ACIDS AT 1000 μg/ml IN SABOROUNDS DEXTROSE AGAR AFTER 48 HR AT 30°

Sl. No.	Compound	Zone of inhibition in mm at 1000 μg/ml				
		1	2	3	4	5
1.	$Cd(OX)_2$	9	7	—	—	7
2.	Cd(OX)(SA)	—	7	—	—	9
3.	Cd(OX)(Cl-SA)	7	10	9	12	7
4.	Cd(OX)(2Br-SA)	9	—	—	8	9
5.	Cd(OX)(2I-SA)	—	8	—	9	9
6.	Cd(OX)($2NO_2$-SA)	7	7	—	—	7
7.	Cd(OX)(Ace-SA)	—	8	—	7	7

Fungi. (1) *Pencillium spp.*, (2) *Asp. niger*, (3) *Tricophyton rubrum*; (4) *Asp. fumigatus*, (5) *Candida albicans.*

TABLE 4—PERCENTAGE EXTRACTION OF METAL INTO CHLOROFORM AT pH 7.4

Sl. No.	Complex	% of cadmium extracted
1.	$Cd(OX)_2$	45
2.	Cd(OX)(SA)	26
3.	Cd(Cl-SA)(OX)	37
4.	Cd(2Br-SA)(OX)	40
5.	Cd(2I-SA)(OX)	42
6.	Cd(NO_2-SA)(OX)	35
7.	Cd(Ace-SA)(OX)	35
8.	$Cd(SA)_2$	7
9.	$Cd(Cl\text{-}SA)_2$	8
10.	$Cd(2Br\text{-}SA)_2$	9
11.	$Cd(2I\text{-}SA)_2$	5
12.	$Cd(2NO_2\text{-}SA)_2$	2
13.	$Cd(Ace\text{-}SA)_2$	2

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Some Anionic Organotellurium Complexes

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Complexes of the formulae $[R_4N]_2^{2+}[C_5H_{10}TeI_2X'_2]^{2-}$ and $[R_4N]^+[p\text{-}C_6H_5\text{-}OC_6H_4TeCl_3X']^-$, where R = CH_3, C_2H_5, C_3H_7 or C_4H_9 ; X' = I, Br or Cl, have been synthesised by refluxing a solution of 1-telluracyclohexane 1 : 1 diiodide or p-phenoxyphenyltellurium trichloride in chloroform with tetraalkylammonium halides in the same solvent The complexes are ionic in nature and have been characterised through analytical, conductance and molecular weight data and nmr spectral studies. The activity of the complexes against certain microorganisms has been tested but not found significant.

COMPLEXES containing dihalo- or tetrahalomono-organyltellurate anions of the formula $[RTeX_3]^-$ and $[RTeX_4]^-$ have recently been reported[1-4]. In continuation of our studies on Lewis acid behaviour of diorganyltellurium dihalides[5,6] we report the synthesis, characterization and antimicrobial activity of some new complexes of the formulae $[R_4N]_2^{2+}$ $[C_5H_{10}TeI_2X_2]^{2-}$ and $[R_4N]^+$ $[p\text{-}C_6H_5\text{-}OC_6H_4TeCl_3X]^-$.

Experimental

1-Telluracyclohexane-1,1-diiodide[7] and *p*-phenoxyphenyltellurium trichloride[8] were prepared by reported methods. Tetraalkylammonium halides were obtained from B.D.H. and used as such. ^{1}H NMR, molecular weight and conductivity data were collected as reported earlier[5].

The desired complexes were prepared (a) by the direct interaction of tetraalkylammonium halides with organotellurium halides and (b) by halogen exchange reaction in certain organotellurium(IV) tetrahalo anions.

(a) 1-Telluracyclohexane-1, 1-diiodide (2 m mol) was refluxed with a solution oftetraalkylammonium salt (4 m mol) in chloroform or dichloromethane (50 ml) for 4-5 hr. Concentration of the reaction mixture followed by addition of petroleum ether (40-60°) afforded the desired complexes which were recrystallised from dichloromethane/petroleum ether (40-60°) mixture.

(b) An aqueous solution of potassium iodide (4 m mol) was added to a solution of tetramethylammoniumtrichlorobromo-*p*-phenoxyphenyltellurate(IV) (0.55 g ; 1 m mol) in 4 *N* HCl with constant stirring. The corresponding tetraiodo compound was precipitated in quantitative yield, filtered, washed with water and air dried.

Analytical data of the complexes prepared are given in Tables 1 and 2.

Results and Discussion

All the complexes are crystalline solids with sharp melting points. Molar conductance values of $10^{-3}M$ solution in acetonitrile lie in the range 208-250 ohm^{-1} cm^2 mol^{-1} for tetrahalocyclohexanetellurates and 124-168 ohm^{-1} cm^2 mol^{-1} for tetrahalo-*p*-phenoxyphenyltellurates. The values correspond to 2 : 1 and 1 : 1 electrolytic behaviour of the complexes, respectively[9]. The observed molecular weights (in nitrobenzene) for tetrahalocyclohexanetellurates are approximately one-third of the calculated value indicating that the complexes are dissociated into three ions in solution, whereas the observed molecular weights of tetrahalo-*p*-phenoxyphenyltellurates are about half of the calculated values showing their 1 : 1 electrolytic behaviour.

Infrared spectra : Infrared spectra of the complexes have been recorded in the region 4000-400 cm^{-1}. Vibrational frequencies associated with the cations are in close agreement with those reported[10] and are not tabulated. Infrared absorption associated with ν(Te–C) lies in the range 530±10 cm^{-1} and is not significantly affected by the nature of the halide groups attached to the metal atom.

^{1}H NMR : ^{1}HNMR spectra of $[(C_2H_5)_4N]_2$-$[C_5H_{10}TeI_2Br_2]$ and $[(C_2H_5)_4N]$ $[p\text{-}C_6H_5OC_6H_4\text{-}TeCl_4]$ were recorded at room temperature. A multiplet in the region δ 3.34-δ 3.12 is observed due to CH_2–N protons whereas a triplet in the region δ 1.27-δ 1.21 may be assigned to $-CH_3$ protons. Two multiplets at δ 3.34 (coupled with CH_2–N protons) are attributed to $-CH_2-$Te and the singlet at δ 2.35 to $-CH_2-$C protons of ring in telluracyclohexane derivatives[11]. Two doublets at δ 7.90 and δ 6.51 are observed due to *m*- and *o*-protons of aromatic ring bonded to tellurium in *p*-phenoxyphenyl derivative[12]. A complex at δ 6.90 may be assigned to phenyl ring (C_6H_5O-) in

TABLE 1—ANALYTICAL DATA OF $[R_4N]_2[C_6H_{10}TeI_2X'_2]$

R	X'	m.p. °C	Yield %	Colour	Analysis%, Found (Calcd) Te	C	H	N	X'	Conductance ohm⁻¹mol⁻¹cm²	Molecular weight, Found (Calcd)
Me	Cl	230	70	White	19 00 (19 04)	23 25 (23.31)	5 01 (5 11)	4.15 (4.18)	48 09 (48 48)	208	215 2 (669.8)
Me	Br	190d	75	Greenish	16 56 (16 79)	20.50 (20 55)	4 55 (4 51)	3.50 (3 68)	54.16 (54 44)	235	240 2 (759 6)
Me	I	128	76	Purple	14 75 (14.94)	18 15 (18.28)	4 00 (4.01)	3 22 (3.28)	59 40 (59.50)	220	415 5 (853.6)
Et	Cl	120	85	Brown	15.90 (16.29)	32 10 (32 21)	6 35 (6 43)	3.55 (3.57)	41 30 (41.47)	210	250 0 (763 0)
Et	Br	175	79	Yellow	14.55 (14 63)	28.80 (28 93)	5 50 (5 78)	3 15 (3 21)	47 02 (47 43)	239	280.6 (871.8)
Et	I	194	72	Brown	13.00 (13 21)	25 99 (26.11)	5 15 (5 21)	2.88 (2.90)	52.50 (52 55)	212	324.8 (965.8)
Pr	I	139-141	80	Brown	10 95 (11 83)	32.00 (32 30)	6.15 (6.17)	2.56 (2 59)	47.00 (47.08)	210	359.3 (1078.9)
Bu	Cl	110	80	Brown	12.50 (12 66)	44 10 (44.11)	8.10 (8.20)	2 70 (2 78)	31.90 (32 23)	250	320.8 (1007.4)
Bu	I	122	68	Brown	10 52 (10 72)	37.20 (37 38)	6 92 (6 94)	2.30 (2 35)	42.16 (42.64)	240	350.0 (1190.0)
*Et	I	194	75	Dark brown	13.15 (13 21)	25.95 (26.11)	5.20 (5 21)	2.80 (2.90)	52.45 (52 55)	210	315.5 (965.8)

TABLE 2—ANALYTICAL DATA OF $[R_4N][p\text{-}C_6H_5OC_6H_4TeCl_3X']$

R	X'	m p °C	Yield %	Colour	Analysis%, Found (Calcd) Te	C	H	N	X'	Conductance ohm⁻¹mol⁻¹cm²	Molecular weight, Found (Calcd.)
Me	Cl	230	70	White	24 56 (24 87)	37.75 (37.46)	4.10 (4.12)	2.68 (2.73)	27 63 (27 73)	140	240.4 (512.9)
Me	Br	172	85	Light yellow	22.70 (22.89)	34 30 (34 47)	3 70 (3 79)	2 45 (2 51)	32 86 (33 44)	151	260.6 (557.3)
Me	I	196	89	Brown	20 95 (21 11)	31.60 (31.79)	3.45 (3 50)	2 29 (2 31)	38.55 (38.63)	150	302.1 (604.3)
Et	Cl	116	80	White	21 90 (22.40)	42.15 (42.21)	5.12 (5.13)	2 42 (2.46)	24.80 (24.95)	124	280.5 (569.4)
Et	Br	113-115	89	Light yellow	20 59 (20.80)	38.96 (39 15)	4 68 (4 76)	2.25 (2.28)	30.25 (30.38)	142	290.2 (613.4)
Et	I	105	81	Brown	19 23 (19 32)	36 27 (36.37)	4.40 (4 42)	2.10 (2.12)	34.90 (35.18)	150	320.2 (660.4)
Pr	I	111-114	90	Brown	17.70 (17.81)	40 20 (40.23)	5.15 (5.20)	1.90 (1.95)	32.40 (32.58)	152	345.2 (716.3)
Bu	I	84	85	Purple	16.45 (16.51)	42 50 (43.52)	5.70 (5.87)	1.75 (1.81)	30.15 (30 22)	142	215.2 (772.6)
*Me	I	159	82	Reddish brown	14.40 (14.53)	21.70 (21 87)	2.30 (2.40)	1 49 (1.59)	57.67 (57 77)	155	480.0 (878 0)
*Et	I	116-117	92	Reddish brown	13.54 (13.66)	25 52 (25 70)	3.10 (3.12)	1.40 (1 49)	53.95 (54.30)	168	467 0 (934.0)

* Anionic complexes obtained by halogen exchange reaction

$[(C_2H_5)_4N][(C_6H_5OC_6H_4TeCl_4]$. The spectra and their integrations correspond to the proposed stoichiometry of the complexes. An octahedral and a square pyramidal structure are tentatively assigned to tetrahalocyclohexanetellurates and *p*-phenoxyphenyltetrahalotellurates, respectively in analogy with previous reports[2-6].

Bio-assay : The antimicrobial activity of the complexes were screened against five bacteria *Streptococcus faecalis, Klebsiella pneumoniae, Escherichia coli, Pseudomonas aerunginosa, Staphylococcus aureus*, and five fungi *Candida albicans, Cryptococcus neoformans, Sprorotrichum schenikii, Trichophyton mentagrophytes, Aspergillus fumigatus.* The complexes show moderate activity towards the bacteria and are inactive against the fungi.

The activity of the complexes (soluble in methanol) was assayed by twofold serial dilution method. The maximum concentration for the tested compound was 100 μg/ml. The fungi was incubated at 28±1° and the bacteria at 37°. The incubation period was 24 hr for all the bacteria and the fungi *Candida albicans, Sprorotrichum schenikii*, 48 hr for *Cryptococcus neoformans* and *Aspergillus fumigatus* and 96 hr for *Trichophyton mentagrophytes. Klebsiella pneumoniae* is affected by all the complexes. *Staphylococcus aureus* (gram positive) appears to be sensitive against *bis*-tetraethyl ammo-

nium tetraiodocyclohexanetellurate. *Bis*-tetramethyl ammonium tetraiodocyclohexanetellurate is active against *Streptococcus faecalis*. All the complexes are completely inactive against gram negative bacteria, *E coli* and *Pseudomonas aerunginosa* and all the fungi used.

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Metal Derivatives of Organoantimony Compounds : Reactions of Anhydrous Chlorides of B(III), V(III) and Sn(IV) with Arylantimony Compounds

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The reactions of anhydrous B(III), V(III) and Sn(IV) chlorides with tetraphenylstibonium chloride, triphenylantimony dichloride and triphenylstibine have been studied. Tetraphenylstibonium chloride is found to form ionic complexes with anhydrous metal chlorides. Triphenylantimony dichloride forms adducts with the chlorides of B(III) and V(III) involving chlorine bridges whereas no adduct has been isolated from anhydrous stannic chloride. The complexes have been characterized by elemental analyses, spectral data (ir and pmr), molar conductivity and magnetic susceptibility measurements.

TAKASHI[1] has studied the reactions of alkylantimony compounds with titanium chlorides. Ionic complexes of the type $[R_4M][R'_2M'X_2]$ or $[R_4M]_2[R'_2M'X_4]$ (where R, R'=CH_3, C_4H_9 or C_6H_5 ; M=N, P, As or Sb ; M'=Sn or Te and X=halo or pseudo-halo anion) have also been reported both from structural as well as biological activity points of view[2-7]. Study of the reactions between organoantimony compounds and titanium(IV) chloride has also been reported from our laboratory[8] and the formation of $[Ph_4Sb][TiCl_5]$, $[Ph_4Sb]_2[TiCl_6]$ and $Ph_3PbCl_2.TiCl_4$ has been confirmed. The work has been extended to the reactions of B(III), V(III) and Sn(IV) chlorides.

Experimental

Anhydrous boron trichloride (Hopkin William ; b.p. 12.5°), vanadium(III) chloride, stannic chloride (B.D.H.) and triphenylstibine (E. Merck) were used as such. Tetraphenyl stibonium chloride[9] and triphenylantimony dichloride[10] were prepared by known methods. Solvents were dried and deoxygenated before use. Because of the hygroscopic nature of some of the reactants and products, all preparations were carried out under anhydrous conditions. The reaction mixtures were flushed with dry nitrogen gas to maintain an inert atmosphere.

General method of preparation of ionic complexes : To a dry benzene or alcoholic solution of anhydrous metal chloride was added slowly and dropwise a benzene or alcoholic solution of tetraphenylstibonium chloride at room temperature under dry nitrogen atmosphere with vigorous shaking. There was no evolution of heat during the course of reaction. The nitrogen gas was passed for 6 to 10 hr and then the flask was stoppered and kept aside for a day or two for complete separation of the solid product. In case of Sn(IV) complex, volume of the reaction mixture was reduced under vacuum. The supernatant solvent was decanted off. The compound was washed successively with dry benzene and dry *n*-hexane and dried *in vacuo* (1-2 mm) at room temperature. The analytical data is given in Table 1.

The reaction of boron trichloride was carried out at 0°.

Preparation of adducts : A benzene or acetonitrile solution of triphenylantimony dichloride was added dropwise to a dry benzene or acetonitrile solution of metal chloride under dry nitrogen atmosphere. There was no change in colour or temperature of the reaction mixture. The mixture was refluxed for 10 to 15 hr. The flask, after cooling, was stoppered and kept aside for a day when a solid compound settled down. Excess of solvent was decanted off and the precipitate was washed with dry benzene (2 to 3 times) and finally with dry *n*-hexane. It was dried *in vacuo* at 70°. The analytical data is given in Table 1.

In case of boron, the compound formed at room temperature. However, no compound formed when anhydrous stannic chloride was reacted with triphenylantimony dichloride.

Physical measurements : Infrared spectra of the compounds (4000-600 cm^{-1}) were recorded in nujol or KBr in Beckman IR-20 spectrophotometer. Far ir spectra of the compounds (600-250 cm^{-1}) were taken using polythene sheets. PMR spectrum was recorded on Perkin-Elmer 90 MHz spectrophotometer in DMSO-d_6. The conductivity measurements were carried out in N,N'-dimethylformamide on an Elico conductivity bridge, type CM-82T. The magnetic susceptibilities were determined on Gouy's balance.

Results and Discussion

The analytical data of the quaternary complexes of boron(III) and vanadium(III) indicated the formation of $[Ph_4Sb][MCl_4]$ [M=B(III) or V(III)] from tetraphenylstibonium chloride and anhydrous

TABLE 1—ANALYTICAL AND CONDUCTIVITY DATA OF THE COMPLEXES

Compound	Colour	m.p. °C	Analysis%, Found (Calcd.) C	H	Cl	ΛM (in N,N'-Dimethyl formamide) mhos $cm^2 mole^{-1}$
$[Ph_4Sb][BCl_4]$	White-crystalline	245(d)	48.26 (49.44)	2.86 (3.43)	25.56 (24.38)	53.2
$Ph_3SbCl_2.2BCl_3$	White	>260	31.84 (32.81)	2 77 (2 27)	42.68 (43.14)	—
$[Ph_4Sb][VCl_4]$	Green	—	45 16 (46.25)	2.96 (3 21)	21.46 (22.81)	75 4
$Ph_3SbCl_2.VCl_3$	Grey	>260	36.18 (37.36)	1.98 (2 59)	31.48 (30.7)	—
$[Ph_4Sb]_2[SnCl_6]$	White-crystalline	195	47.68 (48.36)	3.14 (3 35)	18 68 (17 88)	114.8 50 3*

d = decomposed, * molar conductivity in nitrobenzene.

metal chlorides in the molar ratio of 1 : 1 whereas the complex $[Ph_4Sb]_2[SnCl_6]$ was formed when tetraphenylstibonium chloride and stannic chloride were reacted in molar ratio of 2 : 1.

The adducts of the type $Ph_3SbCl_2.xMCl_3$ [x=1 or 2, M=B(III) or V(III)] were formed when triphenylantimony dichloride was reacted with the chlorides of boron(III) and vanadium(III). Attempts to synthesize the adduct between stannic chloride and triphenylantimony dichloride were unsuccessful.

The reactions of triphenylstibine with vanadium(III) and tin(IV) chloride were studied with a view to synthesizing either triphenylantimony dichloride or obtaining addition products. However, the attempt was unsuccessful. The solid products obtained in these cases after the decantation of the solvent did not show the presence of carbon. The elemental analyses also did not tally with any definite composition. Further, the products were not reproducible. It could be inferred from these observations that a cleavage of the C-Sb bond was probably taking place.

The molar conductance values of the compounds obtained from Ph_4SbCl and metal chlorides (Table 1) indicated them to be 1 : 1 electrolytes for $[Ph_4Sb][MCl_4]$ [M=B(III) or V(III)] and 2 : 1 electrolyte for $[Ph_4Sb]_2[SnCl_6]$. The conductivity of the adducts $Ph_3SbCl_2.xMCl_3$ could not be determined due to their insolubility in common organic solvents.

The infrared spectra of the cations $[Ph_4Sb]^+$ showed bands in the region 450-440 cm^{-1} for carbon-antimony asymmetric stretching frequency[11,12].

For a regular tetrahedral ion $[MCl_4]^-$, there are only two fundamentals which are infrared active, viz., ν_3 and ν_4 which are triply degenerate[13]. In the tetrachloroborate anion $[BCl_4]^-$, three weak bands were observed at 1470, 1380 and 1270 cm^{-1} and two strong bands at 685 and 670 cm^{-1} which could be assigned to $2\nu_3$, $\nu_1+\nu_4+\nu_3$, $2\nu_1+2\nu_4$, ν_3 and $\nu_1+\nu_4$ vibrations, respectively as has been observed by Waddington *et al* for $[POCl_3]^+[BCl_4]^-$ complex[14]. Occurrence of a band at 370 cm^{-1} in the anion $[BCl_4]^-$ suggests distortion in the tetrahedral symmetry which may be due to the ν_1 vibrations[15]. The triply degenerate asymmetric vibrations of the $[VCl_4]^-$ ion occurred at 410 cm^{-1}. This value for the ν(V–Cl) modes is in agreement with the value of 406 cm^{-1} for $[Ph_3MeAs]^+[VCl_4]^-$ reported earlier[16]. Metal-halogen stretching frequency decreases with increasing coordination number of the metal in a given oxidation state. This is consistent with the results observed here.

A regular octahedral molecule gives rise to six normal modes of vibrations. Of these, ν_3 (t1u) and ν_4 (t1u) are infrared active. The ir spectrum of the anion $[SnCl_6]^{2-}$ showed a band at 285 cm^{-1} due to ν_3 vibrations. The assignment of the observed band is comparable with those of other related hexa-halo species[17].

The adducts, $Ph_3SbCl_2.xMCl_3$ were found to be insoluble in the common organic solvents and their melting points were also very high (Table 1). The ir bands of the ligand assigned to phenyl ring vibrations did not undergo any shift on adduct formation[18]. The bands at 440-430 cm^{-1} assigned to νSb–C(Ph) frequency also did not show any shift. Two sharp bands were observed at 730 and 680 due to B–Cl stretching vibrations[14]. The band observed at 350 cm^{-1} in case of $Ph_3SbCl_2.VCl_3$ could be assigned to ν(V–Cl) terminal vibrations. Another band observed at 280 cm^{-1} could be assigned to ν(V–Cl) bridging vibrations. Therefore, a hexacoordinated structure involving chlorine bridges could be assigned to this adduct.

The pmr spectrum of $[Ph_4Sb]_2[SnCl_6]$ in DMSO-d_6 showed complex multiplets in the range δ 7.55-7.85 which were attributed to the aromatic protons of the phenyl rings.

The magnetic susceptibility measurements showed the magnetic moments of $[Ph_4Sb][VCl_4]$ and $Ph_3SbCl_2.VCl_3$ to be 2.76 and 2.71 B.M., respectively[19] indicative of the presence of two unpaired electrons per vanadium atom.

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A Study on Solid State Thermal Decomposition Characteristics of Some Metallo-organic Compounds. Part-I : Dehydration and Decarboxylation of Hydrated Calcium Salts of Pyridine Monocarboxylic Acids

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Solid state dehydration of hydrated calcium salts of picolinic acid, nicotinic acid and isonicotinic acid and subsequent decarboxylation of the corresponding anhydrous salts have been studied by simultaneous TG, DTA and DTG techniques. From the analysis of the TG, DTA and DTG traces for the dehydration of the hydrated salts, the thermal stability order of the hydrates has been found to be $Ca(pic)_2.H_2O > Ca(isoNic)_2.4H_2O > Ca(Nic)_2.3H_2O$. But the trend observed in the decarboxylation process is $Ca(Nic)_2 > Ca(isoNic)_2 > Ca(pic)_2$. Thermal parameters like activation energy, enthalpy change and order of reaction for each process have been computed by standard methods. An attempt has been made to correlate the trend in the thermal stability of the anhydrous salts towards decarboxylation with their molecular structure.

THE calcium salts were prepared by the reaction of a slight excess of $CaCO_3$ (G.R., E. Merck) with the appropriate acids in hot aqueous solutions followed by filtration and subsequent crystallisation.

Simultaneous DTA, TG and DTG determinations of the salts were carried out with a Paulik-Paulik-Erdey type MOM Derivatograph with dry air as the atmospheric gas. The particle size of the samples was in the 100-150 mesh range. The heating rate was about 4.25° per minute and sample size of 180-210 mg was used to make the volume nearly the same in each case. The reference material was aluminium oxide previously heated to 1600°. The sample holder and the reference holder were made of platinum. TG curves were utilised for calculating the activation energies of the processes involved, whereas DTA curves were used to evaluate the enthalpy changes accompanying the reactions. The initial, peak and final temperatures for the dehydration and the decarboxylation processes were noted from the corresponding DTG curves. The hydrated calcium salts and their dehydrated varieties were characterised by recording their ir spectra in halocarbon mull on a Beckman IR 20A model spectrophotometer. All the hydrated and the anhydrous compounds were analysed for calcium by titration with a standard EDTA solution. Carbon, hydrogen and nitrogen were determined by microanalytical techniques.

Results and Discussions

Dehydration process : On gradual heating from room temperature, the hydrated salts were completely dehydrated within the temperature range 39°-240°. From the TG, DTG and DTA traces of the dehydration stage it was found that all the dehydrations occurred in one step. All these processes might be represented by the general equation · $Ca(C_6H_4NO_2)_2.xH_2O = Ca(C_6H_4NO_2)_2 + xH_2O$; when $x=1$, $C_6H_4NO_2^- =$ picolinate ion ; $x=3$, $C_6H_4NO_2^- =$ nicotinate ion ; $x=4$, $C_6H_4NO_2^- =$ isonicotinate ion.

Initial, peak and final temperatures of the dehydration of each species, as obtained from the relevant DTG curves along with the corresponding weight loss are given in Table 1. Enthalpy changes accompanying dehydration of each species were determined by standard methods from the peak area of the corresponding DTA curves using $CuSO_4.5H_2O$ as the standard[1]. Activation energies for each dehydration process were computed from an analysis of the corresponding TG curves using the method of Horowitz and Metzger[2] and the $\ln \ln \frac{W_0 - W_t'}{W - W_t'}$ vs θ plots are presented in Fig. 2. The order of reaction was determined by standard methods[3,4] and was found to be unity. The results obtained are presented in Table 1 and the corresponding curves presented in Fig. 1. IR spectra of the hydrated and the anhydrous varieties were recorded and compared to ascertain the completion of the dehydration process.

Decarboxylation processes : All the anhydrous salts exhibit considerable thermal stability and undergo decarboxylation within the temperature range 340°-600°. Initial, peak and final temperatures for the decarboxylation processes of the anhydrous

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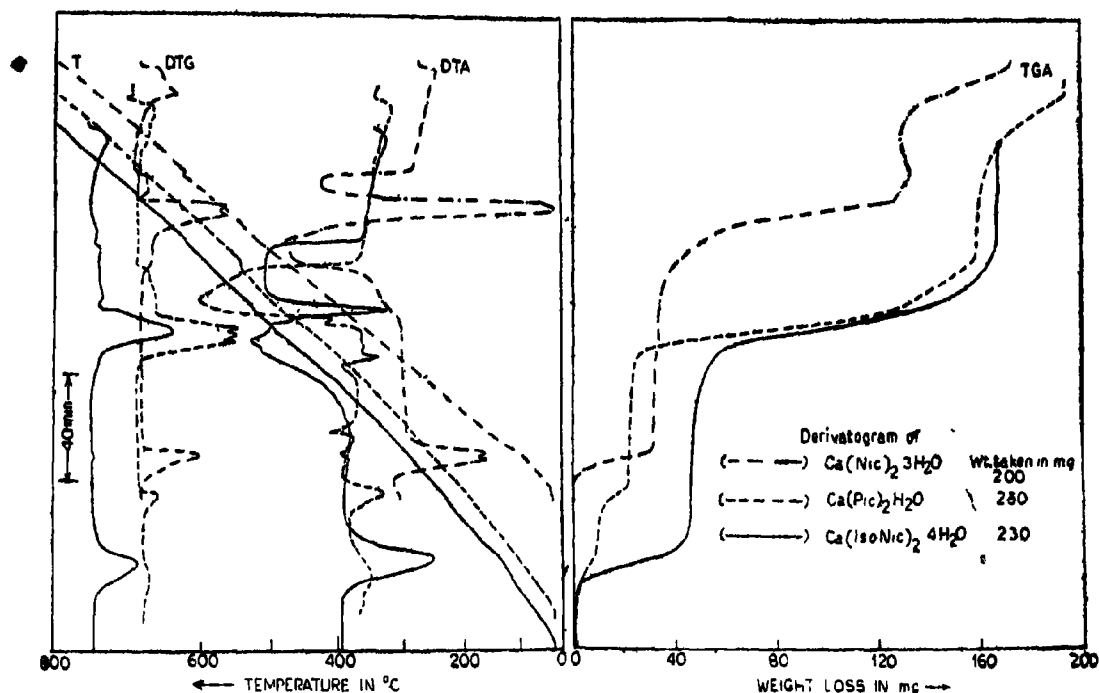


Fig. 1

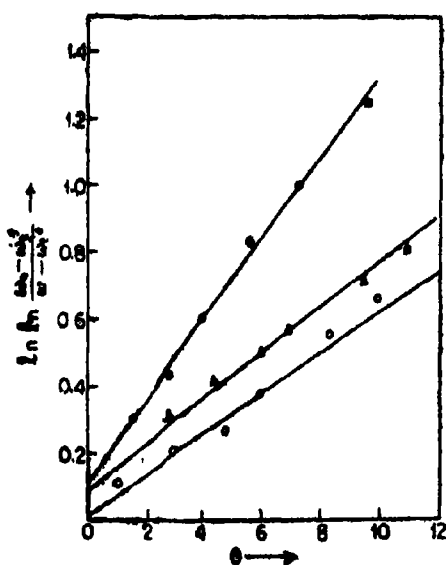



Fig. 2

salts along with the corresponding weight losses are given in Table 2. The final product left in the crucible was found to be $CaCO_3$. This has been confirmed by comparing the X-ray diffraction pattern of the end product with that of a pure $CaCO_3$ sample. Applying the same methods used in the dehydration processes, activation energies of the decarboxylation processes were evaluated from the $\ln \ln \frac{W_0 - W_t^f}{W - W_t^f}$ vs θ plots, given in Fig. 3.

Enthalpy changes accompanying each decarboxylation process were measured from the DTA curves and are presented in Table 2. The order for the decarboxylation reactions was found to be unity in all the three cases. The corresponding curves are presented in Fig. 1.

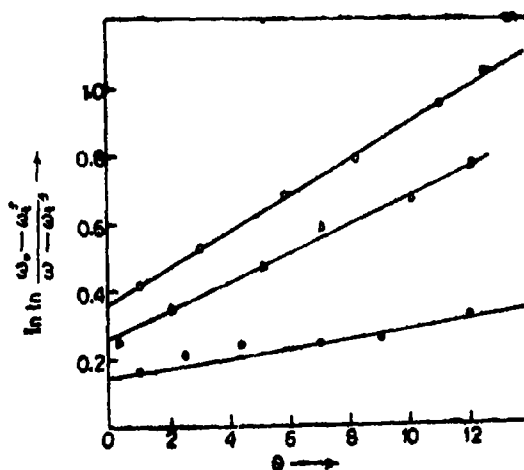



Fig. 3

TABLE 1

Reaction	Initiation temp. °C	Peak temp °C	Completion temp °C	Loss in wt. % Calcd	Loss in wt. % Found	E_{Act} Kcal/mole	ΔH Kcal/mole	Order of reaction
1. $Ca(C_6H_4NO_2)_2.3H_2O \rightarrow Ca(C_6H_4NO_2)_2+3H_2O$ Calcium nicotinate trihydrate	39	90	120	15 97	16	15.55	46.37	1
2 $Ca(C_6H_4NO_2)_2.4H_2O \rightarrow Ca(C_6H_4NO_2)_2+4H_2O$ Calcium isonicotinate tetrahydrate	82	130	215	20 22	20	22.96	62.07	1
3. $Ca(C_6H_4NO_2)_2.H_2O \rightarrow Ca(C_6H_4NO_2)_2+H_2O$ Calcium picolinate monohydrate	160	193	240	5 96	5 88	52.13	26.24	1

TABLE 2

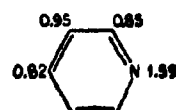
Reaction	Initiation temp °C	Peak temp °C	Completion temp °C	Loss in wt % Calcd.	Loss in wt % Found	E_{Act} Kcal/mole	ΔH Kcal/mole	Order of reaction
4. $Ca(C_6H_4NO_2)_2 \rightarrow CaCO_3$ + products Calcium nicotinate	432	560	622	64 78	60 84	76 14	166 3	1
5 $Ca(C_6H_4NO_2)_2 \rightarrow CaCO_3$ + products Calcium isonicotinate	385	480	620	64.78	64 83	50.85	44.46	1
6. $Ca(C_6H_4NO_2)_2 \rightarrow CaCO_3$ + products Calcium picolinate	380	442	540	64.78	65 38	14 86	20.37	1

Solid state thermal decomposition of the salts of aromatic or heterocyclic acids has received little attention from the kinetic point of view. Most of the workers, who studied the thermal decomposition of the salts of organic acids (mostly aliphatic acids) in the solid state, used the maximum point method[4-6] and the Freeman-Carrol method[7] for the determination of the kinetic parameters. In the present work we have utilised Horowitz and Metzger's method, an analytical technique which utilises a single TG plot to determine the pertinent Arrhenius parameters and reaction order. The values obtained by the application of this method have been verified by the Coats and Redfern[8] method wherever possible. We have utilised the DTA curves for the evaluation of enthalpy changes for the dehydration as well as decarboxylation processes.

The single step dehydration of calcium nicotinate trihydrate and the calcium isonicotinate tetrahydrate indicated that all the water molecules in the nicotinate trihydrate are similarly bound and such is also the case with the water molecules in the calcium isonicotinate tetrahydrate. A single endotherm in each of the DTA curves definitely points to the accuracy of the above conclusion. In the single step dehydration of all the three hydrates represented by the general equation in Table 1, the activation energies and enthalpy changes of dehydration are in the order picolinate > isonicotinate > nicotinate. This difference in thermal stabilities of the hydrates may be attributed to the differences in the mode of binding of the water molecules in the crystals of the three different pyridine monocarboxylates. It may thus be concluded that the water molecules in calcium picolinate are more firmly bound than those in isonicotinate and nicotinate and the water molecules in the calcium isonicotinate are held more strongly in comparison to those present in the calcium nicotinate.

In the decarboxylation of the anhydrous salts represented by equations given in Table 2, the activation energy follows the order nicotinate > isonicotinate > picolinate. The enthalpy change in the decarboxylation process also follows the same order.

It may be concluded from the data in Table 2 that the thermal stabilities of the carboxylates follow the order nicotinate > isonicotinate > picolinate. This trend is quite logical as the negatively charged carboxylate ion has a +I effect[8] and hence releases electrons with a consequent increase of electron density on the ring carbon atom which, if present in a benzene ring, would have stabilized the ring carbon-carboxyl carbon bond. But in the present case, as the ring is a heterocyclic ring, the nitrogen atom being much more electronegative than carbon, would change the situation significantly and we find that unlike benzene, electron density distribution in the pyridine ring[9] is as follows :

0.95 0.85
0.82 N 1.39

Due to the *ortho-para* orienting influence of the carboxylate ion the positions *ortho* and *para* to the ring carbon containing the carboxylate ion will have greater electron density and in the case of calcium picolinate, where the electronegative nitrogen atom is present in the position *ortho* to the ring carbon containing the carboxylate ion, it conveniently draws away this excess electron cloud towards itself and consequently reduces the electron cloud accumulated on the adjacent ring carbon atom considerably. It thus weakens the ring carbon-carboxylate carbon bond to a significant extent making it comparatively thermolabile.

In the case of the 4-picolinate anion, the enhanced electron density in the position *para* with respect to the carboxylate ion is accommodated on the nitrogen atom as a result of which the 4-carbon atom is relieved of some of its electron cloud acquired from the carboxylate anion and results in the weakening of the ring carbon-carboxyl carbon bond and consequently induces thermolability. But overall destabilisation effect is greater in 2-picolinate than in 4-picolinate due to the closeness of the ring nitrogen to the carboxylate substituent in the former and makes the 4-picolinate thermally more stable than the 2-picolinate compound. In the case of the 3-picolinate, the *ortho-para* orienting carboxylate ion would again result in electron enrichment in the *ortho* and *para* positions leaving the *meta* position unaffected. Thus, the increased electron density on the ring carbon atom containing the carboxylate ion is not decreased in this case. This leads to the stabilisation of the ring carbon-carboxyl bond when compared to the 2- and 4-picolinates and makes the 3-picolinate thermally stabler than the other two. Thus, the thermal stability order nicotinate > isonicotinate > picolinate, observed in this study, is quite in accordance with the theoretical principles.

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Stability Constants and Related Thermodynamic Functions of Some Rare-Earth Metal Complexes of Sodium 2-[4-Amino-3-(1,2,4-Triazolylazo)]Naphthol-4-Sulphonate

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The stability constants of La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Yb^{3+} and Y^{3+} complexes of sodium 2-[4-amino-3-(1,2,4-triazolylazo)]naphthol-4-sulphonate have been determined in aqueous medium at different ionic strengths and temperatures employing the Bjerrum-Calvin titration technique as modified by Irving and Rossotti. The free energy, enthalpy and entropy changes involved in complexation have been determined.

THE stability constants of the complexes of sodium 2-[4-amino-3-(1,2,4-triazolylazo)]naphthol-4-sulphonate (ATN-4S) with some rare-earth metal ions have been determined potentiometrically following the Bjerrum-Calvin *p*H-titration technique as modified by Irving and Rossotti[1] and the results are reported in the present communication.

A Beckman Expandomatic SS-2 *p*H meter in conjunction with glass and calomel electrode assembly (0-14 *p*H range) was used for *p*H measurements. Constant temperature was maintained by using a thermostat fitted with a contact thermometer.

Experimental

The synthesis and characterisation of ATN-4S were reported earlier[2]. Its solution was prepared in double distilled water. The nitrates of the rare-earths (99.99% pure) were procured from Indian Rare Earths Ltd., Bombay and their solutions were prepared in double distilled water. In cases where nitrates were not available, the oxides were dissolved in nitric acid, the solutions were heated to dryness and the residues dissolved in double distilled water. All the solutions were standardised complexometrically using EDTA as the titrant. Sodium perchlorate (Riedel) was used to maintain constant ionic strength. A 0.05 *M* standardised solution of tetramethylammonium hydroxide (TMAH) was used as the titrant for potentiometric titrations.

The following solutions (total volume 25.0 ml) were titrated against standard TMAH solution: (i) 1.0 ml $HClO_4$ (0.05 *M*)+1.5 ml $NaNO_3$ (0.02 *M*) +water, (ii) 1.0 ml $HClO_4$ (0.05 *M*)+1.5 ml $NaNO_3$ (0.02 *M*)+10.0 ml ATN-4S (0.05 *M*)+water, (iii) 1.0 ml $HClO_4$ (0.05 *M*)+0.5 ml $Ln(NO_3)_3$ (0.02 *M*)+10.0 ml ATN-4S (0.05 *M*)+water.

All titrations were carried out under nitrogen atmosphere at the desired temperature, maintained with an accuracy of $\pm$ 0.1° and with appropriate amounts of $NaClO_4$ to maintain the desired ionic strengths.

Results and Discussion

The pK_a value of the ligand has been obtained from a plot of log $[\bar{n}_H/(1-\bar{n}_H)]$ vs *p*H and the values obtained at 30° and different ionic strengths, viz., 0.01 *M*, 0.05 *M*, 0.10 *M* and 0.20 *M* are 5.92, 5.85, 5.81 and 5.78, respectively. The pK_a values at 40° and 50° and I=0.10 *M* are 5.71 and 5.61, respectively. The pK_a value at zero ionic strength and 30°, obtained by extrapolation, is 5.96.

The $\bar{n}$ and *p*L data were subjected to the least squares treatment of Sullivan *et al*[3] to give β_n values. The stability constants thus calculated at three different temperatures and I=0.10 *M* are given in Table 1. In cases of ATN-4S complexes, the first two steps involved in complexation proceed almost simultaneously and hence in the case of most metals the step-wise stability constant values for the first two steps cannot be evaluated. Moreover, the lighter elements form only 1 : 2 complexes, while the heavier ones form 1 : 3 complexes also. Hence, log β_2 values are most convenient for comparison as they are available for all the metals used.

A plot of log β_2 vs 1/r (r=ionic radius) shows a regular increase from lanthanum to ytterbium with a break at gadolinium. The position of yttrium lies between gadolinium and terbium. In terms of electrostatic considerations, the gadolinium break may be attributed to the discontinuity of the crystal radius at gadolinium. However, this approach is based on the assumption that the trends in the crystal radii are reflected in the solvated as well as in the coordinated ions, which may not be entirely true[4].

The gadolinium break may be explained in terms of the ligand field theory[5]. Crystal field

effects due to presence of ligand may be operative[5,6], and there may be varying degree of interaction of the 4f orbital with the ligand field. No such stabilisation is expected for the Gd^{3+} ion. Rossotti[7] questioned the validity of this suggestion, since on this basis the stability constants for Y^{3+} and Gd^{3+} complexes should be equal (both ions have no field stabilisations), but due to the smaller size of Y^{3+} ion, Y^{3+} complexes are expected to have higher stability than Gd^{3+} complexes. This has been observed in the present case.

The stability constants of the complexes have been found to decrease with increasing ionic strength of the medium, which is in agreement with the Debye-Hückel equation[8].

The values of stability constants in Table 1 reveals that the stability constant value decreases with increase in temperature. The ΔG, ΔH and ΔS values have been calculated[9] and the results are shown in Table 2. ΔG values have been found to be negative in all cases, showing complex formation to be a spontaneous process. ΔG values have been found to increase with increase in temperature indicating that low temperature favours complexation. This is also confirmed by negative enthalpy values. The positive entropy values show increase in randomness in the systems indicating the presence of a larger number of species. However, the change in entropy for β_3 is negative, which indicates that randomness decreases in going from species ML_2 to ML_3. This might be due to the change in dentate character of the ligand or as a result of the increase in coordination number of the metal ion.

TABLE 1—METAL-LIGAND STABILITY CONSTANTS AT DIFFERENT TEMPERATURES (I=0.10 M $NaClO_4$)

Constant	Temp., °C		
	30	40	50
		La^{3+}	
log β_1	6 16	5 78	5 84
log β_2	11.25	10 68	10 00
		Pr^{3+}	
log β_1	6 71	6 30	5 73
log β_2	12 00	11 39	10.68
		Nd^{3+}	
log β_1	—	6 67	5 84
log β_2	12.49	11 83	11 16
log β_3	15.27	—	—
		Sm^{3+}	
log β_1	—	6 22	4.93
log β_2	12 57	11.80	11.24
log β_3	17.89	14 92	—
		Gd^{3+}	
log β_1	—	—	—
log β_2	12 60	12 04	11.35
log β_3	18.10	15.00	14.42
		Tb^{3+}	
log β_1	—	—	—
log β_2	13.16	12.85	11.68
log β_3	18.96	17.83	15 91
		Dy^{3+}	
log β_1	—	—	—
log β_2	13.74	13.00	12.32
log β_3	19 11	17.85	16 66
		Yb^{3+}	
log β_1	—	—	—
log β_2	14.11	13.39	12.63
log β_3	19.29	17 98	16.70
		Y^{3+}	
log β_1	—	—	—
log β_2	13.13	12.46	11.78
log β_3	18.66	17.28	15 83

TABLE 2—THERMODYNAMIC PARAMETERS OF THE RARE-EARTH METAL COMPLEXES OF ATN-4S AT I=0.10 M $NaClO_4$

Cations	$-\Delta G(\beta_2)$(KJ/mole)			$-\Delta H(\beta_2)$ KJ/mole	$\Delta S(\beta_2)$ (J/deg/mole)
	30°	40°	50°		
La^{3+}	65.27	64 00	61.88	57.90	24 32
Pr^{3+}	69.61	68.32	66 46	57 78	58 86
Nd^{3+}	72.46	70.90	69 00	56 35	53 30
Sm^{3+}	72.91	70 96	68.88	65.48	24.52
Gd^{3+}	74.59	73 00	70 85	66.84	25.58
Tb^{3+}	76.27	74.06	72 22	65.48	35.61
Dy^{3+}	79.70	77.90	76 32	54.84	82.08
Yb^{3+}	81.84	80.23	78.09	59 40	74.09
Y^{3+}	76.17	74.66	72 84	53.33	75.39

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Oxidation Studies. Part—XV : Ag(I)-Catalysis in Oxidation of Amines by Ce(IV) in Nitric Acid, A Kinetic Study

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The kinetics of Ag(I)-catalysed oxidation of methyl, ethyl, isopropyl, *n*-butyl, isobutyl, dimethyl and trimethyl amines by Ce(IV) was studied in nitric acid medium. The Ag(I)-catalysis of Ce(IV)-amine reaction is explained in terms of a 1 : 1 complex formation between Ag(I) and amine which later reacts with Ce(IV) bimolecularly to give the products. The rate law for the Ag(I)-catalysed oxidation of amines was found to be

$$-\frac{d[Ce(IV)]}{dt}=\frac{kK[Ce(IV)][amine][Ag(I)]}{1+K[amine]+K[Ag(I)]}$$

Ammonia and the corresponding aldehyde or ketone were identified as the products of oxidation of aliphatic primary amines, while formaldehyde and other amines were the products when dimethyl or trimethyl amines were the substrates. The activation parameters for the oxidation of amines are presented and discussed.

IT is reported that amines could be oxidised using oxidants like permanganate[1], lead tetraacetate[2], *cobaltic perchlorate*[3] *and chlorinedioxide*[4]. Recently, we reported[5] the kinetics of oxidation of amines by Ce(IV) in nitric acid medium. It was shown in all these cases that amines could be oxidised by two distinct mechanisms, one involving dehydrogenation and the other by an attack at the lonepair electrons on nitrogen in the rate determining step. Even though Ag^+ ions were found to be good catalysts, only sporadic references have been made in the literature about their use as catalyst in the oxidation of organic compounds by Ce(IV), specially in HNO_3 medium. In view of this, we have taken up a systematic kinetic study of oxidation of amines by Ce(IV) in presence of Ag^+ to find out whether the presence of Ag^+ ions results in a change in the mechanism of oxidation as also the mechanism of catalysis.

Experimental

All the chemicals used were of reagent grade. The method of following the kinetics was the same as reported earlier[6]. Approximate amount of ceric ammonium nitrate (AnalaR) was weighed and dissolved to give a $\sim$0.10 *M* solution. The concentration was estimated by titrating against standard ferrous ammonium sulphate. This solution was diluted with nitric acid (0.50 *M*) to give 0.01 *M* solution. Salts of the general formula $R.CH_2NH_3^+NO_3^-$ were prepared by mixing one mole of amine with one mole of nitric acid. The silver nitrate used as catalyst was also of AnalaR grade

Ammonia and corresponding aldehydes or ketones were the products of Ag^+-catalysed oxidation of aliphatic amines while formaldehyde and other corresponding amines were the products when the dimethyl or trimethyl amines were used as substrates. Ammonia was detected with Nessler's reagent. Formaldehyde and corresponding aldehyde *or ketone were identified by their characteristic* tests[7] and further confirmed by m. p. of their 2,4-DNP derivatives.

Results and Discussion

Under the conditions of [Ce(IV)] $\ll$ [amine] in the presence of constant amount of Ag(I) the order in [Ce(IV)] was found to be unity. The pseudo first order rate constants (k') were calculated from *the slope of the linear plots of* $\log [a/(a-x)]$ vs time [where, a and a$-$x are the concentrations of Ce(IV) at zero and time t, respectively]. The order in [amine] obtained from the plots of log k' vs log [amine] was found to be fractional. Increase in [Ag(I)] increased the rate and the order in [Ag(I)] was also fractional in all the cases (Table 1). Increase in $[H^+]$ or $[NO_3^-]$ decreased the rate of oxidation (Table 2). The reactions were studied in the temperature range 313-333°K to evaluate the activation parameters. Typical results with methylamine as the substrate are given in Tables 1 and 2 and Fig. 1. Induced polymerisation was observed when acrylamide was added to the reaction mixture.

Wylie employed[8] the solvent extraction technique and suggested the existence of $H_2[Ce(NO_3)_6]$ in moderately strong nitric acid solutions. Shorter[9], who studied the oxidation of acetone by ceric nitrate in nitric acid assumed that $Ce(OH)^{3+}$ was the reactive species. Similar conclusions were drawn by Mathur and Bakore[10,11] in the oxidation of *sec*-butanol and *iso*-propanol. However, Sethuram and Muhammad[6] and Santappa and Sethuram[7] concluded from the effect of $[NO_3^-]$ and $[H^+]$ on the rate of oxidation of formaldehyde and some alcohols in nitric acid medium that the neutral $Ce(NO_3)_4(H_2O)_2$ was the most likely

TABLE 1—EFFECT OF [Ag(I)] ON k' IN Ce(IV)-ALIPHATIC AMINE REACTIONS CATALYSED BY Ag(I)

[Ce(IV)]=0.005*M* ; [HNO_3]=0.500 *M* ; Temp.=333°K ;

Amine	$k' \times 10^3$ min^{-1} at [Ag(I)] mol dm^{-3}							
	0.010	0.015	0.020	0.080	0.040	0.050	0.060	0.080
Methyl (0.40 *M*)	6.10	–	8.69	–	13.9	–	19.8	25.8
Ethyl (0.80 *M*)	–	13.0	17.7	21.0	26.4	–	35.9	–
n-Propyl (0.20 *M*)	7.08	–	10.1	–	13.4	–	19.2	25.1
iso-Propyl (0.10 *M*)	2.65	–	5.00	–	9.60	–	12.0	16.8
n-Butyl (0.10 *M*)	14.8	–	20.8	26.4	31.0	39 5	–	–
iso-Butyl (0.40 *M*)	–	26.7	32.0	39 1	49.0	–	57.0	–
Dimethyl (0.20 *M*)	–	20.0	34.8	50.6	60.7	72.4	79.4	–
Trimethyl (0.10 *M*)	10.7	–	14.0	17.8	21.4	23.7	–	–

TABLE 2—EFFECT OF [NO_3^-] AND [H^+] ON Ce(IV)-*n*-PROPYLAMINE REACTION CATALYSED BY Ag(I)

[Ce(IV)]=0.005 *M* ; [HNO_3]=1.00*M* , [Ag(I)]=0.020 *M* , [*n*-propylamine]=0.200 *M* , Temp.=328°K

[Salt] or [Acid] mol dm^{-3}	$k' \times 10^3$ min^{-1} (NO_3^-)	$k' \times 10^3$ min^{-1} (H^+)
0.400	22 4	20.4
0.800	16.6	17.0
1.20	12.6	13 9
1.60	10.2	11 7
2.00	8 70	10.0
2 40	5 90	9.00

reactive species of Ce(IV). The probable species that could exist in nitric acid solutions of Ce(IV) are $Ce(NO_3)_6^{2-}$, $Ce(NO_3)_5^-$, $Ce(OH)(NO_3)_4^-$ and $Ce(NO_3)_4$ at fairly high [nitrate ion]. The choice of the reactive species was rather difficult but the fact that the rate of oxidation of amines by Ce(IV) in nitric acid was retarded by NH_4NO_3 coupled with the fact that the oxidation in perchloric acid medium was inhibited by the addition of nitrate ions indicated that the reactive species might be the neutral ceric nitrate molecule $Ce(NO_3)_4$ or more correctly $Ce(NO_3)_4(H_2O)_2$. The presence of

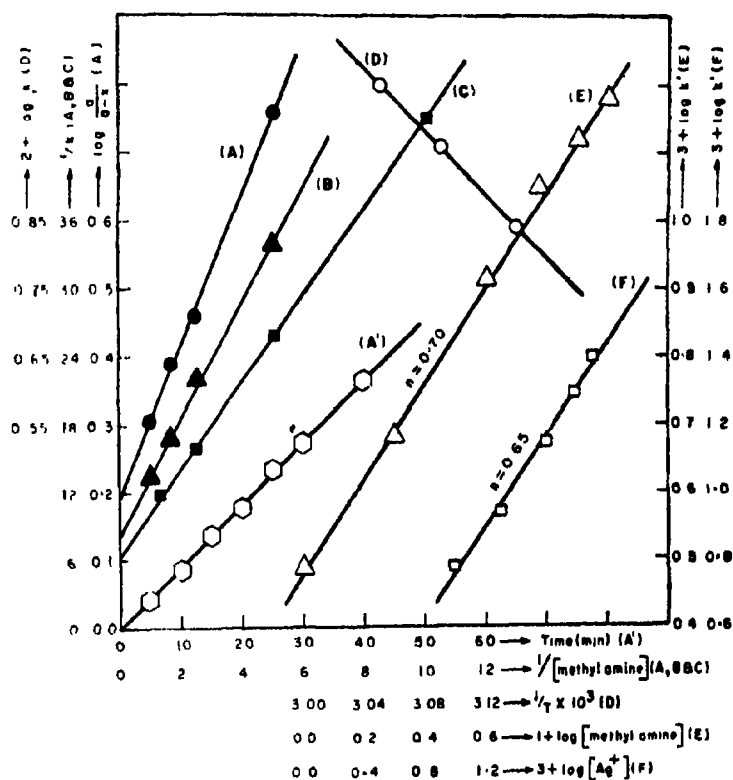



Fig. 1

(A')—Plot of log [a/a-x] vs time, [Ce(IV)]=0.005 *M*, [HNO_3]=0.500 *M*, [Ag(I)]=0.020 *M*, [methylamine] =0 800 *M* ; temp.=333°K

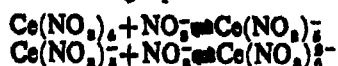
(A, B and C)—Plots of 1/k' vs 1/[methylamine] at temp. 318, 328 and 328°K, respectively [conditions same as in (A')]

(D)—Plot of (2+log k) vs (1/T×10³) [conditions same as in (A')]

(E)—Plot of (3+log k') vs (1+log[methylamine]) [conditions same as in (A')]

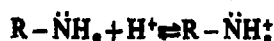
(F)—Plot of (3+log k) vs (3+log [Ag^+]) [conditions same as in (A')]

species $[Ce(OH)(H_2O)(NO_3)_4]^-$ could not be discounted, though at high acid concentrations employed in the present work these hydroxylated species could be neglected. The inverse dependency of rate on $[NO_3^-]$ may be explained if one assumes neutral $Ce(NO_3)_4$ to be the reactive species according to the following equilibria

$$Ce(NO_3)_4 + NO_3^- \rightleftharpoons Ce(NO_3)_5^-$$
$$Ce(NO_3)_5^- + NO_3^- \rightleftharpoons Ce(NO_3)_6^{2-}$$

In the presence and absence of Ag^+ it was found that H^+ ions inhibit the reaction. This could be either due to the hydrolysed species acting as the reactive species

$$Ce(NO_3)_4(H_2O)_2 \rightleftharpoons [Ce(NO_3)_4(OH)H_2O]^- + H^+$$

or due to the presence of equilibrium of the type

$$R-\ddot{N}H_2 + H^+ \rightleftharpoons R-\dot{N}H_3^+$$

with $R-\ddot{N}H_2$ as the reactive species. To find out whether hydrolysed species is the reactive one, we have studied the effect of $[H^+]$ on the oxidation of *n*-propanol, where the protonation equilibrium is not likely. It was found that increase in $[H^+]$ increases the rate of oxidation of *n*-propanol indicating clearly that hydrolysis equilibrium exists and that neutral ceric nitrate is the reactive species. Since [Ce(IV)] and $[HNO_3]$ are the same in the amines oxidation, we believe that in this case also the unhydrolysed species is the reactive one. The inhibition of H^+ ions on the amines oxidation could therefore be attributed to the removal of reactive free amine by protonation.

It was reported[8] that in the absence of Ag(I) the order in [amine] is unity. The fractional order in [amine] in presence of Ag(I) indicated that it may be involved in complex formation either with Ce(IV) or Ag(I). Spectral studies in the present study indicated no complexation between Ce(IV) and aliphatic amine in conformity with our earlier observations[8]. Induced polymerisation due to the addition of acrylamide indicated the formation of the free radicals. Ag(I) is known to form colourless adducts with organic compounds[18]. Therefore, the formation of an adduct between Ag(I) and amine, before oxidation by Ce(IV) in a slow step to yield Ag^{2+}-amine adduct, is proposed. If the adduct formation is taken as the first step, the reaction scheme for Ce(IV)-amine reaction in the presence of Ag(I) could be written as follows:

$$R-CH_2-\ddot{N}H_2 + Ag(I) \overset{K}{\rightleftharpoons} (adduct)^+$$

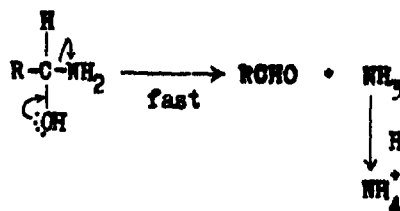
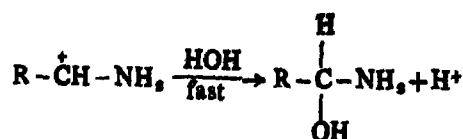
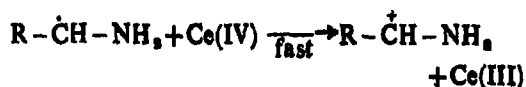
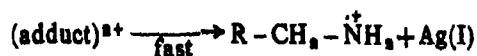
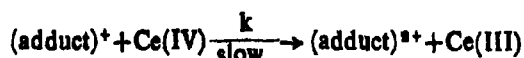
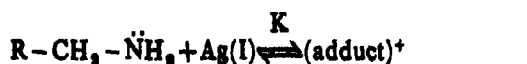
$$(adduct)^+ + Ce(IV) \xrightarrow[slow]{k} (adduct)^{2+} + Ce(III)$$

$$(adduct)^{2+} \xrightarrow{fast} R-CH_2-\dot{\overset{+}{N}}H_2 + Ag(I)$$

$$R-CH_2-\dot{\overset{+}{N}}H_2 \xrightarrow{fast} R-\dot{C}H-NH_2 + H^+$$

$$R-\dot{C}H-NH_2 + Ce(IV) \xrightarrow{fast} R-\overset{+}{C}H-NH_2 + Ce(III)$$

$$R-\overset{+}{C}H-NH_2 \xrightarrow[fast]{HOH} R-\underset{OH}{\overset{H}{C}}-NH_2 + H^+$$

$$R-\underset{:OH}{\overset{H}{C}}-NH_2 \xrightarrow{fast} RCHO + NH_3 \xrightarrow{H^+} NH_4^+$$

From the above mechanism, the rate equation comes out to be

$$-\frac{2.303\, d\log[Ce(IV)]}{dt} = k'$$
$$= \frac{kK[amine][Ag(I)]}{1+K[amine]+K[Ag(I)]} \quad (1)$$

where k' is the observed pseudo first order rate constant, k the bimolecular rate constant for the slow step and K the formation constant of Ag(I)-amine adduct. Equation 1 accounts for the observed fractional order dependence of rate in [amine] and [Ag(I)]. At constant [Ag(I)], we get the equation 1 modified as below:

$$\frac{1}{k'} = \frac{1}{[amine]}\left[\frac{1}{kK[Ag(I)]} + \frac{1}{k}\right] + \frac{1}{k[Ag(I)]} \quad \ldots (2)$$

It is clear from equation 2 that plots of 1/k' vs 1/[amine] at constant [Ag(I)] should be linear. Such plots were obtained in the present work for all the amines studied (Fig. 1). From the intercept and slope values, the bimolecular rate constants, k, and the formation constants, K, for Ag(I)-amine adduct were evaluated at different temperatures and the various activation parameters calculated (Table 3).

TABLE 3—ACTIVATION PARAMETERS FOR Ce(IV)-AMINE REACTION CATALYSED BY Ag(I)

Amine	$k \times 10^2$ $dm^3 mol^{-1} sec^{-1}$ (at 323°K)	K ($dm^3 mol^{-1}$)	E_{exp} (kJ mol^{-1})	$\Delta H^{\ne}$ (kJ mol^{-1})	$\Delta G^{\ne}$ (kJ mol^{-1})	$-\Delta S^{\ne}$ J deg^{-1} mol^{-1}
Methyl	1.78	1.40	45.0	42.3	90.6	113
Ethyl	3.27	3.12	77.0	74.3	89.0	45
n-Propyl	3.79	4.33	44.0	41.3	88.6	146
n-Butyl	5.25	4.98	59.5	56.8	87.7	96
iso-Propyl	5.95	6.98	76.5	73.8	87.4	42
iso-Butyl	4.17	6.15	63.5	60.8	88.3	85
Dimethyl	18.5	9.20	44.8	42.1	84.3	130
Trimethyl	5.90	6.70	72.5	69.8	87.4	54

It was observed in the present study that the electron releasing groups accelerate the formation of adduct between Ag(I) and aliphatic amine, the order of reactivity being Me < Et < *n*-prop < *n*-but < *i*-but < *i*-prop. It was also observed that increase in the length of the carbon chain of amine had little effect on K whereas increase in the number of methyl groups on α-carbon atom had a significant effect (Table 3). These results could explain the

ease of formation of adduct between Ag(I) and aliphatic amine as the α-carbon atom to the amine group becomes more and more electron rich. This in turn facilitates the reaction between the adduct and Ce(IV) in the rate determining step.

Applicability of Taft's equation :

To study the applicability of Taft's equation for all the primary amines log K values were plotted against σ^* values at 323°K according to the general equation

$$\log(K/K_o) = \rho^* \sigma^* + \delta E_s \quad \ldots (3)$$

where K and K_o represent the formation constants of Ag(I)-adducts of substituted amines and methylamine, respectively, σ^* and E_s the polar and steric substituent constants, and ρ^* and δ the reaction constants for the same two effects, respectively. Using the standard least square method of bivariant linear regression[18] the reaction constants due to the polar ρ^* and steric δ effects were found to be -3.37 ± 0.04 and -0.195 ± 0.02, respectively. It was found that the formation constants for all the amines studied could satisfactorily be fitted into equation 3, using the above values. From the values of the reaction constants ρ^* and δ it is evident that the polar effects are playing a major role in the formation of the adduct compared to the steric effects.

The activation parameters for all the amines studied may be explained on the basis of isokinetic relationship. The ΔH^* and ΔS^* are related by the equation $\Delta H^* = \Delta H_0 + \beta \Delta S^*$ where β is the isokinetic temperature. In the present study the plot of ΔH^* vs ΔS^* (Table 3) was linear with a slope equal to 380°K which is the isokinetic temperature, β, for this reaction series. The value is found to be much above the temperature range used (313-333°K) in the present study suggesting that the reactions are enthalpy controlled.

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Studies in Triethylamine-Water. Part—IV : Predicting the Solubilities of Triethylamine and Water

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The solubility curve of the binary system triethylamine-water, which has a lower critical solution temperature of 18.3°, is predicted from simple thermodynamics by analysing the vapour pressure data. In this method, the equation for g^E (the molar excess free energy of mixing) of amine-water systems is assumed to hold good for temperatures at which the system is only partially miscible. The common tangential points on the curves of g^M (the molar free energy of mixing) vs X (the solvent composition, expressed in mole fraction of Et_3N in water), drawn as isotherms, reproduce the experimental solubility curve of the binary system within ±2 per cent.

THE solubility curve of the binary system triethylamine-water has been experimentally studied by a number of workers[1-11]. The effect of ion size on the phase separation of the binary system has been brought out by comparing the effect of about 80 electrolytes on the phase separation temperature (PST) of this binary solvent mixture[12]. Phase separation effects in the ternary system Et_3N-water-KI have been quantitatively predicted[13] by using the hydration numbers of K^+ and I^- ions, obtained from conductance studies of KI in this solvent mixture[14]. In the present work, the solubility curve of the binary system Et_3N-water is predicted from simple thermodynamics by analysing the vapour pressure data available in literature[4,15-27].

Method :

The excess molar free energy of mixing, g^E, of a binary mixture can be calculated from the observed molar free energy of mixing, g^M, using the equations :

$$g^M = g^I + g^E \quad (1a)$$

$$g^I = RT(1-X)\ \ln(1-X) + RT\ X\ \ln X \quad (1b)$$

where g^I is the ideal molar free energy of mixing. g^M is calculated from vapour pressure measurements:

$$g^M = RT(1-X)\ \ln(p_1/p_1^0) + RT\ X\ \ln(p_2/p_2^0) \quad (2)$$

where R is the gas constant, T is the absolute temperature, p_1 and p_1^0 are the vapour pressure of water in solution and in pure form, respectively at temperature T, p_2 and p_2^0 are the vapour pressure of Et_3N in solution and in pure form, respectively at temperature T, X is the mole fraction of Et_3N in the binary mixture.

When g^M is plotted against the mole fraction of Et_3N for various temperatures, the common tangential points of the isotherm give the compositions of the coexisting phases. When the compositions of these coexisting layers are plotted against temperature, the course of the variation of these points gives the solubility curve of the binary system.

This method needs the vapour pressure data for temperatures at which the binary system is not completely miscible (in fact it is impossible to have data at these temperatures practically). Copp and Everett[16] have proposed a fitting equation for g^E by modifying the one proposed by Guggenheim[28]. By considering only the first nine terms, the equation becomes

$$g^E/RT = AX\ (1-X) + X\ (1-X)(1-2X)\ [B + C\ (1-2X) + D(1-2X)(1-X)^6] \quad (3)$$

In Et_3N-water system, equation (3) reproduces the g^E within ±1 cal in the homogeneous regions.

The following simple assumptions are made to obtain the g^E for temperatures above the lower critical solution temperature (LCST) of Et_3N-water system :

(i) Equation (3) holds good for temperatures at which the system is heterogeneous.

(ii) Since the terms A, B, C and D of equation 3 all show a linear dependence on temperature below LCST in the homogeneous phase, they are considered to have the same dependency at temperatures above LCST in heterogeneous regions also.

Vapour pressure data :

Vapour pressures for Et_3N-water mixtures have been reported by various authors[4,15-27]. Chun and coworkers[20] have fitted their experimental g^E to equation 3 and have reported the values of the terms A, B, C and D for homogeneous solutions below LCST of the binary solvent mixtures.

Results and Discussion

The values of A, B, C and D against temperature have been plotted (Fig. 1) and extrapolated to temperatures upto 23°. The extrapolated values of these terms are given in Table 1. g^E is calculated
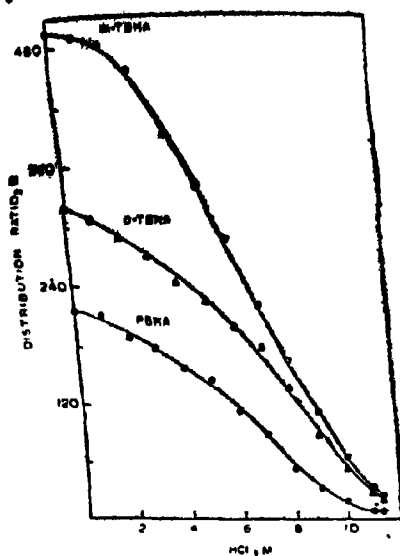
Fig. 1. Distribution ratio, D, of N-arylhydroxamic acids between $CHCl_3$ and aqueous HCl.

TABLE 1—VALUES OF THE TERMS A, B, C AND D OF EQUATION 3 AT VARIOUS TEMPERATURES ABOVE LCST

Temp °C	A	B	C	D
19	2.442	0 1985	0.579	1.016
20	2.456	0 2015	0.590	1.034
21	2.470	0 2045	0 602	1 050
22	2.483	0.2075	0.613	1.066
23	2 498	0.2105	0.624	1.084

TABLE 2—VARIATION OF g^M WITH SOLVENT COMPOSITION X AT VARIOUS TEMPERATURES

X	$-g^M$ (cals.mol^{-1}) Temp. °C 19	20	21	22	23
0.01	8.88	8.67	8.45	8.23	8.00
0.02	11.45	11.92	10.58	10.17	9.71
0.04	13.06	12.25	11.46	10.69	9.84
0.06	13.68	12.54	11.45	10.40	9.38
0.08	14.35	13.02	11.69	10.43	9.04
0.10	15.42	13.92	12.42	10.11	9.40
0.15	19.47	14.69	15.89	14.19	12.30
0.20	24.34	22.43	20.48	18.65	16.60
0.30	33.62	31.61	29.59	27.68	25.51
0.40	41.45	39.43	37.50	35.64	33.49
0.50	47.98	46.11	44.22	42.47	40.40
0.60	52.75	51.00	49.23	47.58	45.65
0.70	55.30	53.70	52.08	50.59	48.83
0.80	55.88	54.06	52.70	51.46	50.02
0.90	50.07	49.27	48.48	47.65	46.78

using equation 3 and g^M is calculated with equation 1. Table 2 gives the values of g^M for different temperatures. g^M vs X isotherms are drawn and the common tangent points are obtained from these isotherms (Fig. 2). Fig. 3 shows the course of the variation of the common tangential points obtained at various temperatures (Table 3).

The variation of the common tangential points of g^M-X isotherms reproduces the solubility curve of Et_3N-water system given by Kohler and Rice[9],
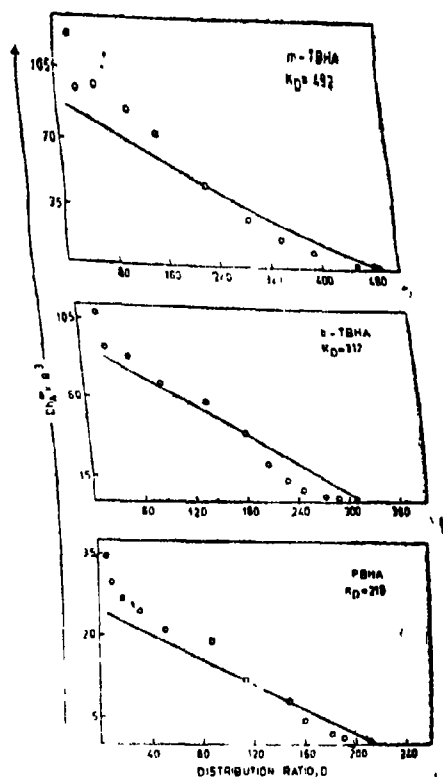
Fig. 2. Estimation of K_D ($CHCl_3$ and aqueous phase)
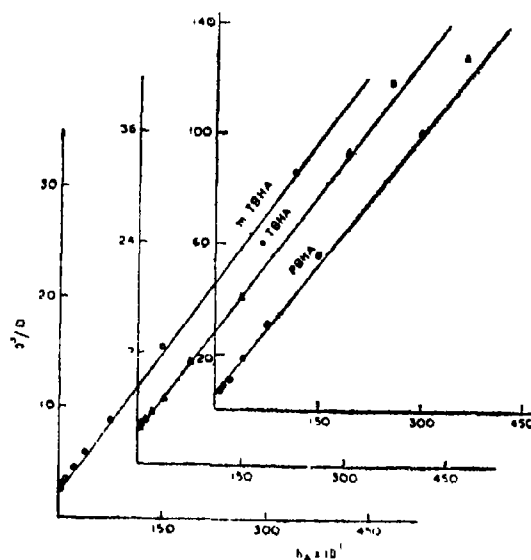
Fig. 3. Estimation of K_D, chloroform and aqueous phase.

who had taken special care in the purification of the solvents. Copp and Everett[15] have used this procedure to work out the solubility curve of the system methyldiethylamine-water. But in their work they assumed that the terms B, C and D are temperature independent. The curve obtained in

TABLE 3—PREDICTED VALUES OF THE COMPOSITIONS OF THE COEXISTING PHASES 1 AND 2 AT VARIOUS TEMPERATURES

X=Mole fraction of Et_3N

Temp. °C	X_1	X_2
19	0.030	0.200
20	0.028	0.275
21	0.026	0.375
22	0.025	0.475
23	0.020	0.535

their analysis showed a second minimum, which is absent in the experimental curve. In the present work, there is no such anomaly for Et_3N-water system. The solubility curve is reproduced within ±2% of the experimental values.

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Studies on Electrolysis in a W-tube with Reference to Non-Faradaic Behaviour*

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Electrolysis of a dilute aqueous solution at low current density in a W-tube, though associated with high volume deficit, is nearly free from coliberation; its occurrence, if at all, being limited to the anode gas only. Unlike the electrolysis in a U-tube, two sharp and stationary boundaries formed in the intermediate zone of the W-tube may act as barriers to the migration of the ions responsible for the non-*Faradaic phenomenon of coliberation.*

IT was observed by Palit[1,2] that if an alcoholic solution of an ionic dye or a dilute aqueous solution of $K_2Cr_2O_7$ is electrolysed in a double-bent U-tube (called a W-tube), two very sharp boundaries appear inside the two inner tubes, dividing the solution into three zones as: anode - acidic dark coloured - neutral colourless - alkaline light coloured - cathode. Such phenomenon in a W-tube was also observed later by other workers[3]. Since electrolysis in a W-tube shows such intriguing features (depletion in the intermediate zone in violation of Hittorf mechanism of current conduction), it was considered interesting to examine the extent to which the W-tube shows non-Faradaic behaviour[4,5]. The earlier observations on non-Faradaic electrolysis were confined to U-tube only. The results reported in this paper also show the effect of cell geometry on non-Faradaic electrolysis.

Experimental

The W-tube used for the electrolysis is shown in Fig. 1. Electrodes used are bright platinum foils
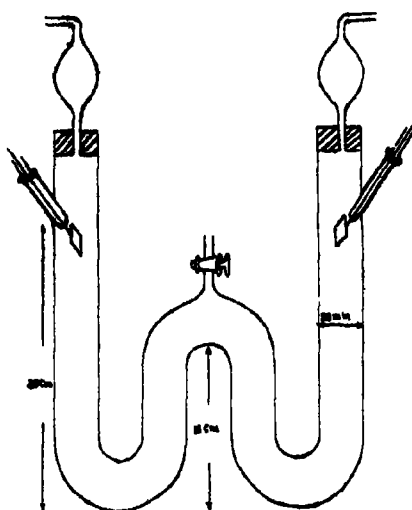
Fig. 1.

($1 cm^2$). Like U-tubes[6], the arms of the W-tube are also connected to gas burrettes for collection of the liberated gases at the anode and the cathode. A coulometer containing 1.0 N K_2SO_4 solution was connected in series. Current was passed either from D. C. mains (230 volts) or D. C. power supply unit. At the beginning, 2 mA current was allowed to pass but with the progress of electrolysis, he current density decreased to a very small value (a few hundred μA) due to depletion of ions from the middle portion of the W-tube. The electrolysis was, therefore, allowed to run for several days so that a measurable amount of gas could be collected over the electrodes. Liberated gases were then analysed by sparking with the help of a tesla coil.

Results and Discussion

The results are given in Fig. 2 and they are discussed with a comparison with those obtained in a U-tube under otherwise identical conditions.

(*i*) *Electrolysis of salt solution* (0.001 N): With dilute solution of sodium sulphate or potassium sulphate, the results become very much different from those in a U-tube and the salient features are:

(a) High volume deficit (less than 50% of the total gas is liberated) and almost no coliberation on either side. Small amount of gas is evolved at the intermediate zone of the cell.

(b) Current falls to a very low value with the progress of electrolysis because the ions gradually get removed from the middle portion of the tube.

0.001 N $K_2Cr_2O_7$ solution also does not give coliberation on either side but the deficit is not as high as with potassium or sodium sulphate solution.

Electrolysis of 0.01 N Na_2SO_4 solution gives completely Faradaic results which is also very unlikely during electrolysis in a U-tube.

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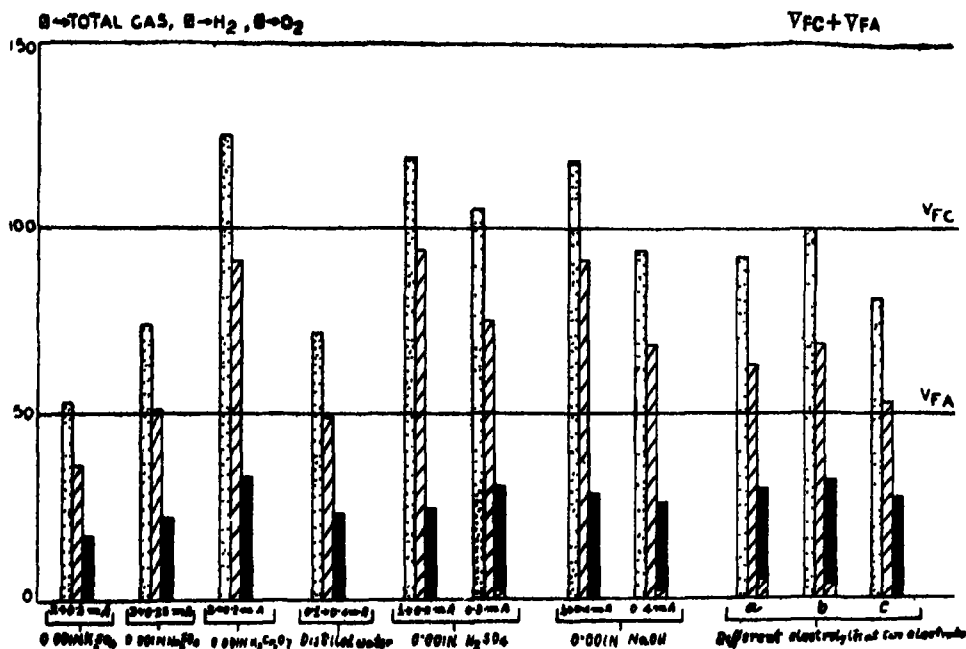
Fig 2. Results of electrolysis in a W-tube Of the three jointed columns, the left one (dotted) represents the total volume of gases liberated, the middle one the volume of gas at the cathode, and the right one that at the anode The striped and the darkened parts in the middle and the right columns represent the volume of hydrogen and oxygen respectively in the mixture of the two.

a = 0 001 N NaOH at cathode and distilled water at anode, b = Distilled water at cathode and 0.001 N H_2SO_4 at anode, c = 0.001 N NaOH at cathode and 0.001 N H_2SO_4 at anode.

(ii) *Electrolysis of water :* With pure water, the volume deficit, though very high, is less than what is found with the salt solutions and a remarkable observation is that the anode gas explodes on sparking while the cathode gas remains totally free of coliberation.

(iii) *Electrolysis of 0.001*N *sulphuric acid solution :* At the beginning when some acid still remains near the cathode, no coliberation takes place on either side. With progress of electrolysis, as the acid concentration at the cathode side diminishes, the anode gas explodes on sparking while the cathode gas is pure hydrogen. However, the percentage of coliberation at the anode side is not very high.

(iv) *Electrolysis of 0.001* N *sodium hydroxide :* Results are similar to those observed in the experiment with 0.001 N H_2SO_4.

(v) *Electrolysis of two different electrolytes at the cathode and the anode :* Few experiments were done by using alkali/acid, water/acid or alkali/water separately in the two compartments.

(a) *(C) alkali-acid (A) :* With 0.001 N NaOH at the cathode side and 0.001 N H_2SO_4 at the anode side, the results are similar to those obtained with 0.001 N salt solutions. There is no coliberation either at the cathode gas or at the anode gas and volume deficit is also very high.

(b) *(C) water-acid (A) :* Distilled water at the cathode side and 0.001 N H_2SO_4 at the anode side give results different from those in the previous set up. The anode gas remains explosive while the cathode gas is free from any coliberation. Volume deficit is not very remarkable.

(c) *(C) alkali-water (A) :* Results similar to those in set up (b) are obtained with 0.001 N NaOH at the cathode side and distilled water at the anode side.

Conclusion : So far, the results with U-tube led us to believe that electrolysis at low current density and low concentration always produces non-Faradaic features, particularly deficit and coliberation. The results with W-tube brings forth the inadequacy of the above tenet. Here is a cell geometry where, though the current density and the concentration are both low, the deficit is extraordinarily high but there is no coliberation of the cathode gas in almost all cases, and whatever coliberation there is, it is limited only to the anode gas. These features are probably connected with boundary formation as is observed with many dyes. Since electrolysis in a W-tube shows a very intriguing behaviour mainly formation of two sharp and stationary boundaries separating the solutions into three zones : A/acid-water-alkali/C, it may be assumed that the intermediate zone somehow acts as a barrier to the ions which are responsible for the coliberation at cathode. If we presume these ions to be H_3O^+, they are likely to get discharged at the centre with production of some H_2O_2. This explains why in such experiments the

hydrogen-oxygen stoichiometry is unbalanced in favour of hydrogen. The observations reported in this paper also lend support to the contention[6] that water getting charged at the electrodes and carrying a part of the current is responsible for non-Faradaic behaviour.

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Study of Dielectric Properties and Dipole Moments of Mn(II) Salts of Some Fatty Acids in Benzene Solutions

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The dipole moments of Mn(II) salts of palmitic, stearic and oleic acids were calculated by the methods of Gopalkrishna, Smyth-Dasgupta, Halverstadt-Kumler and Guggenheim. The values were calculated by Cole-Cole plots and parameters ϵ_0, ϵ_∞ and α were determined. From the plots of log τ vs 1/T, ΔH, ΔF and ΔS were evaluated. In the present investigation, dipole moment values obtained by Gopalkrishna method compared favourably with those obtained by Guggenheim method.

THE present author has reported several studies on dipole moments and dielectric and other properties of salts of fatty acids. These include dipole moments and relaxation studies on Cu(II) stearate[1], Cu(II) oleate[2], pyridine adducts of salts of fatty acids[3], effect of the salts of fatty acids on $KMnO_4$[4-6] and others[7,8].

The present paper envisages to cover the dipole moments and dielectric relaxation properties of Mn(II) in all its aspects employing all possible recognised methods in literature. The initial problem faced by a worker in such studies is the sorting out of dielectric loss due to direct current conduction and one due to absorption. The present author being naturally interested in the latter conducted studies to ascertain whether the loss was due to absorption alone. This will be clear from Table 1 which gives the data involved in the well known expression :

$$\sigma = 5.5 \times 10^{-13} \, f \, \epsilon'' \text{ ohm}^{-1}\text{cm}^{-1}$$

where σ = specific conductance
f = frequency in Hertz
ϵ'' = the dielectric loss observed.

Since log ϵ''/log f ratios in the present investigation (Table 1) are far from unity, it was concluded that the losses observed here are due to absorption alone.

TABLE 1—LOG f AND LOG ϵ'' VALUES

Temp. °C	$f \times 10^{-3}$	ϵ''	log f	log ϵ'' (−ve)
	System :	Manganese palmitate-benzene		
34	260.0	0.2163	5.4150	0.6649
	272.5	0.0893	5.4354	1.0493
70	260.0	0.2082	5.4150	0.6815
	267.5	0.1160	5.4273	0.9351
	System :	Manganese stearate-benzene		
34	265.0	0.0984	5.4232	1.0068
	272.5	0.1147	5.4354	0.9408
70	260.0	0.2808	5.4150	0.6360
	275.0	0.0436	5.4393	1.3602
	System :	Manganese oleate-benzene		
34	257.5	0.2040	5.4108	0.6904
	265.0	0.1061	5.4232	0.8743
70	260.0	0.1272	5.4150	0.8955
	270.0	0.0762	5.4314	1.1181

Experimental

The salts were prepared by double decomposition method from the sodium salts of the fatty acids and the chloride of the metal, the latter added in slight excess. However, the purest salts were prepared by the method described earlier[3]. The elemental analysis of the salts is in good agreement with the calculated values.

The dielectric constant, ϵ', and dielectric loss, ϵ'' were measured on DK–06 WTW decameter as described earlier[1]. The values of ϵ_0 and ϵ_∞ were obtained from the Cole-Cole plots of dielectric constant ϵ' vs dielectric loss ϵ'' on X axis[9]. The values of relaxation time were calculated using the expression

$$\frac{u}{v} = \omega\tau^{(1-\alpha)}$$

where v = distance on the Cole-Cole plot between ϵ_0 and experimental point,
u = distance on the Cole-Cole plot between ϵ_∞ and experimental point.
ω = angular frequency.

The enthalpy, ΔH, entropy, ΔS, and molar energies, ΔF, were calculated from the plots of ln τ vs 1/T using Eyring's equation. All the relevant data involved in these methods are set out in Table 2.

TABLE 2—THERMODYNAMIC QUANTITIES AND THE RELEVANT DATA AT TEMPERATURES 34, 50, 60 AND 70° FOR Mn(II) PALMITATE, STEARATE AND OLEATE IN THAT SERIAL ORDER. (ΔH, ΔF AND ΔS IN Kcal/mole)

Temp. °C	ϵ_0	ϵ_∞	α	τ	
34	2.2696	2.2589	0.08	2.13	ΔH = 2.50
50	2.2891	2.2385	0.08	2.82	ΔF = 9.99
60	2.2205	2.2125	0.27	3.05	ΔS = −0.044
70	2.2140	2.2044	0.13	3.42	
34	2.2590	2.2513	0.40	2.88	ΔH = 3.54
50	2.2814	2.2814	0.14	1.97	ΔF = 9.88
60	2.2225	2.2135	0.24	2.19	ΔS = −0.0185
70	2.2078	2.1967	0.05	1.23	
34	2.2345	2.2289	0.18	2.57	
50	2.2035	2.1926	0.18	2.05	ΔH = 3.51
60	2.1864	2.1778	0.27	2.06	ΔF = 9.78
70	2.1646	2.1564	0.82	1.80	ΔS = −0.02

Thermodynamic quantities, ΔH, ΔF, and ΔS, are given in the last column of Table 2.

TABLE 3—DIPOLE MOMENT VALUES [μ(D)] OF Mn(II) SALTS OF PALMITIC, STEARIC AND OLEIC ACIDS BY SMYTH-DASGUPTA'S (1), GOPALKRISHNA'S (2), HALVERSTADT-KUMLER'S (3) AND GUGGENHEIM (4) METHODS AT 34, 50, 60 AND 70°

Compound	Temp. °C	μ(D) (1)	(2)	(3)	(4)
$MnPT_2$	34	3.62	3.50	3.48	3.50
	50	3.85	4 16	1.45	4.08
	60	3.12	3.16	1.54	3 29
	70	3.63	4.19	2.35	3.92
$MnST_2$	34	6.57	6.34	—	5 53
	50	7.32	4.90	—	5.96
	60	7.74	5.57	6.29	6 23
	70	8.67	6.04	10.18	6 63
$MnOL_2$	34	1.97	—	—	5.65
	50	2.26	—	—	5.81
	60	2.66	—	—	5 72
	70	3.39	—	—	5.12

Results and Discussion

The methods of Gopalkrishna[10], Smyth-Dasgupta[11], Halverstadt-Kumler[12] and Guggenheim[13] were used to evaluate dipole moments of the salt at 34, 50, 60 and 70°. The Cole-Cole plots of dielectric constant ϵ' vs dielectric loss ϵ'' gave the values of ϵ_0 and ϵ_∞ on the X axis, which were used for calculating the μ values by the methods of Gopalkrishna and Smyth-Dasgupta.

Literature indicates that there is a great scope in determining the μ values of these salts, since a few salts like magnesium palmitate and calcium oleate[14] and magnesium oleate[15,16] have been studied and the dipole moment values reported are quite divergent. Palit *et al*[17] have used the Guggenheim equation for the determination of μ values of metal salts of fatty acids.

Guggenheim equation was modified by Palit and Banerjee[18] for a rational approach to the problem of computation of polarization and is given as :

$$P_2\mu = \frac{3M_2}{di\,(\epsilon_{1+2})^2} \cdot \left[\left(\frac{\delta}{\delta W_2}\,(\epsilon - n^2)\right)\right]_0$$

The attractive feature of the Guggenheim method could be retained without sacrificing the accuracy perceptibly.

Since the dipole moment values showed a slightly erratic trend, a search was made to ascertain whether the solutions were colloidal. No such behaviour was noticed when a cone of light was passed through the 10^{-4} *M* solutions with the help of an arc appliance supplied with VNI SPECK constant deviation spectrometer.

In the present studies, the dipole moments are obtained by recent methods, namely those of Gopalkrishna and Smyth and Dasgupta. The μ values obtained by these two methods have consistently agreed with each other and have also been in agreement with those obtained by the Guggenheim method. In Gopalkrishna's method, two plots are constructed to evaluate μ values which are interdependant. The values are very susceptible to the values of $[(\epsilon_0 - \epsilon_\infty)]$ which are obtained from Cole-Cole plots. Halverstadt-Kumler method suffers from the serious defect of measurement of densities of solutions.

Hence it was concluded that the changes in μ observed may be attributed to viscosity changes[8] in the benzene solutions of the salts. A rough estimate would be that if the viscosity increases with temperature, the orientation of the molecules will hinder and there will be fall in dipole moment. In the case of $MnPT_2$ solutions the flow time was observed to decrease in the temperature interval of 60~70°. As against this, it was seen to increase in $MnOL_2$ (60°~70°) and decrease in $MnST_2$ (50°~60°). Another explanation lies in the mesomorphic changes observed in the acids themselves which is carried to their salts.

Sydow[19] has investigated the mesomorphic forms in the fatty acids from their ir spectra in the range of 0-13μ. Sindaire *et al*[20] have observed in their studies of ir spectra of saturated hydrocarbons and esters of fatty acids that at least the two forms differ with respect to crystal axis. Phase transition was reported in some of the salts of fatty acids by X-ray diffraction.

The dipole moment values of palmitic, stearic and oleic acids are extremely small[21-23] and do not indicate any relationship between the chain length and the μ values. However, in the present investigation, the chain length is found to play a major role in that generally the dipole moment order[24] is $MnST_2 > MnPT_2 > MnOL_2$. This observation has been made by others in similar salts of magnesium. It is probable that the negative charge on the oleate, palmitate and stearate anions is distributed over the whole of the anion, much the same way as an electron cloud in an orbital, and hence the centre of gravity of charge lies further from the positive charge on the cation as the length of the chain goes on increasing. This may account for the order of μ as $MnST_2 > MnPT_2 > MnOL_2$.

The distribution parameter, α, is found to be dependent on the length of the chain and double bonded structure and increases generally with temperature. The entropy values, ΔS, are negative indicating an orderly orientation of these Mn(II) salts. This means free molar energies of these salts are larger than their enthalpy values. Again, the low values of ΔS suggest that the molecules of the Mn(II) salts must be orienting themselves as a whole without segments or cations in them taking any prominent part.

Chitoku and Higasi[25] have stated that if the molecular shape is spherical or vary but a little from the spherical shape, the relaxation times are slightly dependent on the viscosity of the medium. They, however, observed that if the molecules are asymmetrical in shape its dipole rotation in the

medium automatically involves displacement of vast number of neighbouring molecules and as a result the relaxation times depend markedly on the viscosity of media. Some calculations on Mn(II) salts studied here, carried out according to O'Dweyer and Sack method[26], show that the values differ largely from unity (a condition for spherical molecules) which according to these workers is a sure indication of asymmetry in the molecule.

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Studies on the Interfacial Tension and Electrical Conductance of Oil/Water Emulsions Stabilized by Lignosulphonate of *Eucalyptus teriticornis*

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Kerosene/water and turpentine/water emulsions stabilized by lignosulphonate have been prepared. Their interfacial tension and electrical conductance have been measured and discussed as a function of emulsifier concentration, temperature, salinity, alcohol-carbon chain length, emulsification time with temperature and phase volume ratio.

IT is generally accepted that higher concentration of lignosulphonate, carbon chain length of alcohols and temperature lower the interfacial tension but increase the conductance and make the emulsions more conductive. Literature reveals that oil/water emulsions have been prepared by employing soaps[1], Indian gums[2], surfactants[3], protiens[4], saponins[5] etc., as emulsifiers and their properties such as interfacial tension[6], surface tension and viscosity[7], particle size[8], stability[9], creaming[10], phase inversion[11] etc. have also been studied. The effect of phase-volume ratio on the physico-chemical properties of oil/water emulsions, dielectric constants[12] etc. has also appeared in literature. In the present investigations attempts have been made to assess the emulsifying power of lignosulphonates, a waste product of paper industry, by measuring the interfacial tension and electrical properties of kerosene/water and turpentine/water emulsions stabilized by this product. A correlation of interfacial tension with the conductance of emulsions has also been made.

Experimental

Double distilled kerosene (sp. gr. 0.7948), turpentine (sp. gr. 0.8745) and water having conductance 1×10^{-6} ohm^{-1} cm^{-1} were used in all the experiments. The alcohols viz., methanol, ethanol, *n*-propanol, *n*-butanol, pentanol, and sodium chloride used were of B.D.H. AR grade. The lignosulphonate from eucalyptus wood was prepared at Star Paper Mill, Saharanpur and at Cellulose and Paper Branch, Forest Research Institute, Dehradun.

Preparation of emulsion and measurement of its conductance : Oil/water emulsions have been prepared by taking kerosene and turpentine as internal phase in the following manner :

1. Keeping the concentration of lignosulphonate constant (0.5%) and varying the oil/water ratio viz., 10 : 10, 10 : 20, 10 : 30, 10 : 40, 10 : 50, 10 : 60, 10 : 70, 10 : 80 and 10 : 90.
2. Keeping the oil/water ratio (1 : 3) and concentration of lignosulphonate (0.5%) constant and varying the emulsification temperature viz., 20, 30, 40, 50 and 60° alongwith the emulsification time viz., 0.5 1, 2, 4, 8 and 12 min, respectively.
3. Keeping oil/water ratio (1 : 3) and the concentration of lignosulphonate (0.5%) constant and adding 0.1% of alcohols viz., methanol, ethanol, *n*-propanol, *n*-butanol and pentanol.

Emulsions were prepared by agent-in-water method[13] and the conductance was measured with a sensitive conductivity bridge instrument.

Measurements of interfacial tension : The interfacial tension of different concentration of lignosulphonate in water viz., 0.01, 0.02, 0.04, 0.08 and 0.1% and the salinity effect by adding different concentrations viz., 0.01, 0.02, 0.04, 0.08, 0.1, 0.12, 0.16, 0.20 and 0.24% of NaCl to 0.05% lignosulphonate solution, have been measured against kerosene and turpentine oils by drop-volume method[14,15], respectively.

The effect of various alcohols i.e. methanol, ethanol, *n*-propanol, *n*-butanol and pentanol on the interfacial tension of 0.05% aqueous solution of lignosulphonate against kerosene and turpentine have also been measured by keeping alcohol concentration constant (0.1% v/v) and calculated by the equation : $\gamma_{ow} = \frac{V(d_1-d_2)g\times F}{r}$, where, γ_{ow} is the interfacial tension, V the volume of single drop, d_1 and d_2 the densities of respective phases, g the gravity, r the radius of the dropping tip and F is the correction factor[16]. All the results have been presented in Figs. 1 to 4 and Tables 1 to 5.

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TABLE 1—EFFECT OF TEMPERATURE ON THE INTERFACIAL TENSION OF OIL/0.05% AQ SOLUTION OF LIGNOSULPHONATE

Temp. °C	Interfacial tension (Dynes/cm)	
	Kerosene/water	Turpentine/ water
20	11.24	8.58
25	10.99	8.43
30	10.83	8.18
35	10.50	7.98
40	10.18	7.78

TABLE 2—EFFECT OF PHASE-VOLUME RATIO ON THE CONDUCTANCE OF O/W EMULSIONS

Lignosulphenate = 0.5%, Temp. = 25 ± 1°

O/W Ratio	Conductance × 10^{-3} $ohm^{-1} cm^{-1}$	
	Turpentine/water	Kerosene/water
10 : 10	5.68	3.47
10 : 20	7.80	4.80
10 : 30	8.92	5.47
10 : 40	10.98	6.88
10 : 50	12.40	7.40
10 : 60	14.10	8.44
10 : 70	16.80	8.97
10 : 80	17.92	9.74
10 : 90	18.05	10.53

TABLE 3—EFFECT OF EMULSIFICATION TEMPERATURE AND TEMPERATURE ON THE CONDUCTANCE OF O/W EMULSIONS

O/W Ratio = 1 : 3, Lignosulphonate concn 0.5%

Temp. °C	Emulsification effect Conductance × 10^{-3} $ohm^{-1} cm^{-1}$		Temperature effect Conductance × 10^{-3} $ohm^{-1} cm^{-1}$	
	Kerosene/ water	Turpentine/ water	Kerosene/ water	Turpentine/ water
20	9.04	14.2	8.53	11.80
30	9.53	14.8	12.62	14.85
40	9.89	15.1	14.51	16.02
50	10.20	15.7	16.39	17.7
60	10.83	16.3	17.80	19.1

TABLE 4—EFFECT OF ALCOHOL CARBON CHAIN LENGTH ON THE CONDUCTANCE OF O/W EMULSIONS

Lignosulphonate concn : 0.5% ; O/W Ratio 1 : 3 ; Alcohol 0.1%

Alcohol	Conductance × 10^{-3} ohm^{-1} cm^{-1}	
	Kerosene/water	Turpentine/water
CH_3OH	11.70	15.2
C_2H_5OH	11.74	15.4
n-C_3H_7OH	11.79	15.8
n-C_4H_9OH	11.81	15.95
$C_5H_{11}OH$	11.85	16.05
$C_6H_{13}OH$	11.89	16.3

TABLE 5—EFFECT OF EMULSIFICATION TIME ON THE CONDUCTANCE OF O/W EMULSIONS

O/W Ratio 1 : 3, Lignosulphonate = 0.5% ; Temp. = 25 ± 1°

Emulsification time (min)	Conductance × 10^{-3} $ohm^{-1} cm^{-1}$	
	Kerosene/water	Turpentine/water
0.5	10.05	13.8
1.0	10.69	14.2
2.0	10.91	14.9
4.0	11.34	16.5
8.0	12.56	18.3
12.0	12.57	18.31

Results and Discussion

The interfacial tension of kerosene/water and turpentine/water interfaces against varying concentrations of lignosulphonate (Fig. 1) depict a
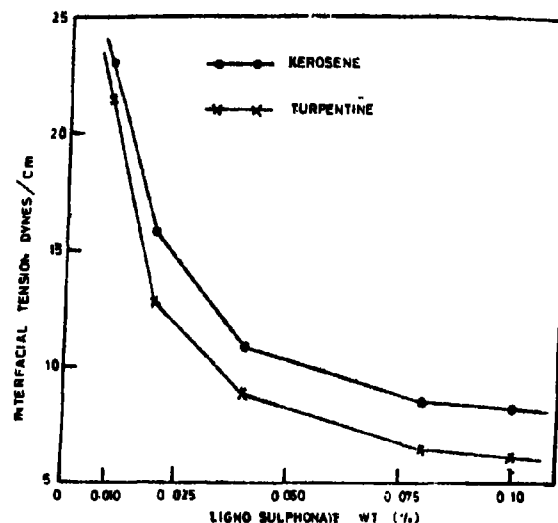
Fig. 1. Effect of lignosulphonate concentration on the interfacial tension of oil/water emulsions

decrease in surface tension of emulsions with an increase in lignosulphonate concentration. In both the cases, the decrease is linear at concentration 0.08% and beyond. This lowering of interfacial tension is attributed to the adsorption of lignosulphonate at oil/water interface and as adsorption reaches a constant value due to the formation of monolayer, the lowering in interfacial tension becomes smaller and smaller[17].

Fig. 2 indicates a decrease in the interfacial tension of oil/water emulsion with an increase in
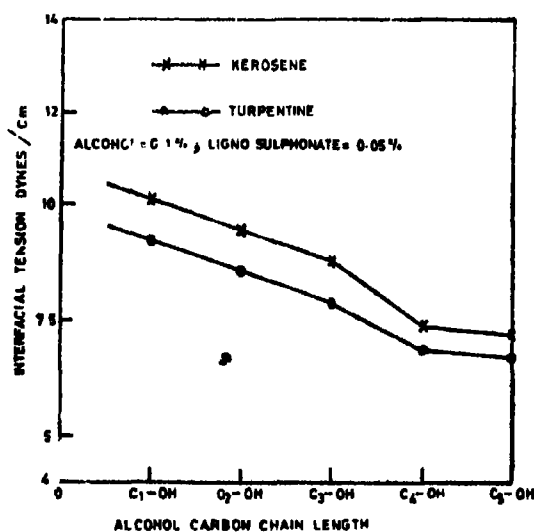
Fig. 2. Effect of alcohol carbon chain length on the interfacial tension of oil/water emulsions.

the carbon chain of alcohol. A break is observed on passing from n-propanol to n-butanol. This is expected as less soluble alcohols (in water) solubilize more oil and consequently lower the interfacial tension[13]. Fig. 3 shows the rise and fall in interfacial tension with increasing sodium chloride concentration. The temperature shows an adverse effect on interfacial tension, the decrease being linear with rise of temperature. This is in harmony with the results of earlier workers[14].

It is clear from Fig. 4 that conductance increases with an increase in the concentration of emulsifier, while Table 2 indicates a fall in the conductance of emulsion with increasing phase-volume ratio. This may be attributed to an increase in the number of droplets with the increase in phase-volume ratio.

At higher emulsifier temperature the emulsions appear to be more conducting (Table 3). However, in some cases, emulsions first prepared at room temperature show an increase in conductance in the temperature range 20° to 60°. This may be due to an increase in the mobility of oil-droplets.
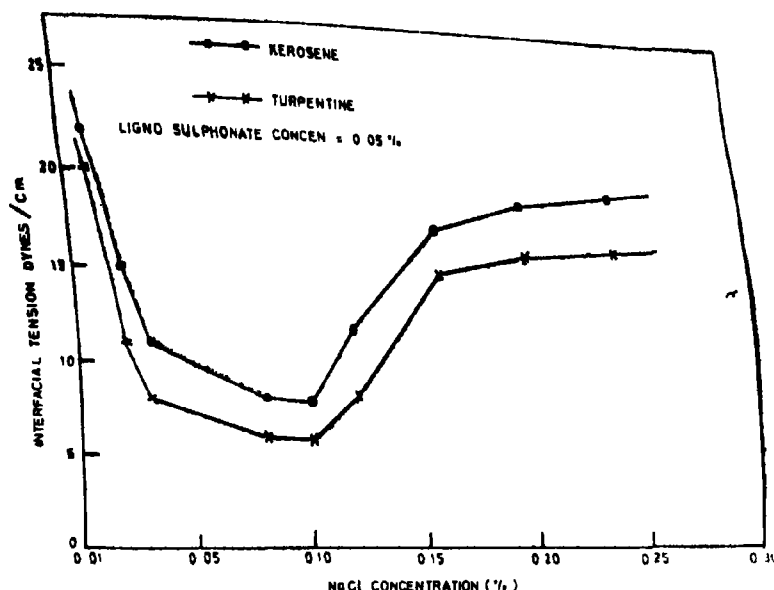
Fig. 3. Effect of salinity on the interfacial tension of oil/water emulsions.

Fig. 4. Effect of lignosulphonate concn. on conductance of oil/water emulsions.

Tables 4 and 5 present the effect of alcohol carbon-chain and emulsification time on the conductance of kerosene/water and turpentine/water emulsions. It is evident that as the carbon chain of alcohols and emulsification time increase, the conductance of emulsions also increases. It can thus be concluded that emulsions having lower interfacial tension show higher conductance values.

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Polarographic Studies on the Reduction of the Azomethine Bond in Aryl Thiosemicarbazides and the Determination of Hammett Parameters

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The reduction of 4-phenyl substituted thiosemicarbazides gave one, 2-electron transfer, well defined, irreversible, diffusion controlled reduction waves. The studies were made in Britton-Robinson buffer (pH range 2.0-11.0). The reduction in these compounds takes place at azomethine bond, formed due to a change in structure in alkaline medium. The effect of substituents on the reduction site and its correlation with Hammett substituent constants (σ x) have been studied. A possible mechanism for their reduction at DME has been proposed.

THE polarographic behaviour of sulphydryl compounds at the dropping mercury electrode has been studied[1,2] intensively during the past few years. Since this class is one of the most important among biologically important compounds, its oxidation reduction potential is of much importance. Thiosemicarbazides, well known precursors of antituberculous[3], antifertility[4] and antineoplastic agents, have not been studied polarographically so far.

The present communication deals with the polarographic reduction of these compounds and the effect of various substituents on its half-wave potential and its correlation with the Hammett substituent constant (σ x).

Experimental

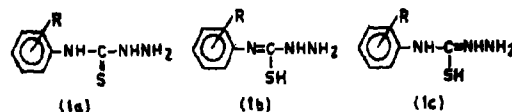
Preparation of thiosemicarbazides : The 4-phenyl substituted thiosemicarbazides, having substituents hydrogen, 2-methyl, 3-methyl, 4-methyl, 2-methoxy, 3-methoxy, 4-methoxy, 2-chloro, 3-chloro, 4-chloro, 2-ethoxy and 2, 5-dimethyl, were prepared according to the method given in literature[5].

Solutions : 0.01 *M* stock solutions of 4-phenyl substituted thiosemicarbazides were freshly prepared in dimethylformamide. Britton-Robinson buffers[6] and 1 *M* KCI solution were prepared in double distilled water from AnalaR grade chemicals.

Apparatus : Polarographic curves were recorded using a Cambridge pen recording polarograph. The capillary used possessed the characteristics 3 75 $mg^{2/3}$ $S^{-1/2}$ at a zero applied voltage. For the determination of the *p*H value of the solutions ELICO *p*H meter model LI-10, fitted with a glass-electrode was used. The number of electrons consumed in the electrode process was determined by the millicoulometry method of DeVries and Kroon[7] in a small volume (0.3 ml) using a mercury pool as cathode.

Results and Discussion

The polarographic behaviour of all these 4-phenyl substituted thiosemicarbazides was studied in the *p*H range 2.0-11.0. One well developed reduction wave was observed for all these compounds at *p*H above 7.0. The slope of $E_{1/2}$ vs *p*H plots for all these thiosemicarbazides lie in the range 0 060-0.067 V/*p*H, which indicates that all substituted thiosemicarbazides reduce by similar mechanism. However, no wave was obtained below *p*H ~7.0 This can be accounted for on the basis of change in structure in alkaline medium. Thio form of thiosemicarbazides (**Ia**) changes into thiol form (**Ib** or **Ic**). Such changes of thio form to

(Ia) R-C6H4-NH-C(=S)-NHNH2   (Ib) R-C6H4-N=C(SH)-NHNH2   (Ic) R-C6H4-NH-C(SH)=NNH2

thiol form in alkaline medium have also been reported by other workers[8]. Since the change in structure produce $-C=N-$ as a site for facile reduction, the polarographic wave is obtained only in alkaline medium.

All these thiosemicarbazides reduce in a one, 2-electron transfer, diffusion controlled reduction waves. A few typical polarograms have been depicted in Fig. 1. The change in $E_{1/2}$ with increasing concentrations of depolarizer suggests the irreversible nature of the waves (Table 1). The diffusion character of the limiting current has been proved by the linear dependance of the wave height on the concentration of thiosemicarbazides and by the proportionality of the wave height to the square root of the mercury column.

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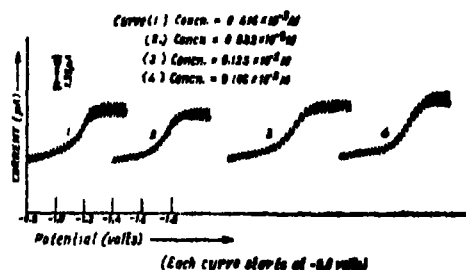
Fig. 1. Polarograms of o-tolylthiosemicarbazide at various concentrations

TABLE 1—HALF-WAVE POTENTIALS OF 4-PHENYLTHIOSEMICARBAZIDES AT VARIOUS CONCENTRATIONS

(R-C₆H₄)-NH-C(=S)-NHNH₂

No	R	Concentrations 0.416 × 10^{-3} *M* $E_{1/2}$ (V)	0 832 × 10^{-3} *M* $E_{1/2}$ (V)	0.125 10^{-2} *M* $E_{1/2}$ (V)	0.166 × 10^{-2} *M* $E_{1/2}$ (V)
I	H	−1.20	−1.20	−1.26	−1.28
II	2-CH_3	−1.20	−1 20	−1 27	−1 30
III	3-CH_3	−1 22	−1 26	−1 30	−1 31
IV	4-CH_3	−1.20	−1.26	−1 30	−1 34
V	2-OCH_3	−1 20	−1 28	−1.30	−1 32
VI	3-OCH_3	−1 20	−1 21	−1.28	−1 30
VII	4-OCH_3	−1 22	−1 22	−1 28	−1 30
VIII	2-Cl	−1 26	−1.28	−1 32	−1.34
IX	3-Cl	−1 26	−1 30	−1 38	−1.40
X	4-Cl	−1 26	−1 31	−1 35	−1 37
XI	2-OC_2H_5	−1.34	−1 36	−1 38	−1.39
XII	4-OC_2H_5	−1 22	−1 26	−1 29	−1.32
XIII	2,5-$(CH_3)_2$	−1.29	−1.26	−1 30	−1 32

The following mechanism based on two electron transfer can be proposed for the reduction of azomethine bond in these thiosemicarbazides. Similar reduction steps of the reduction of semicarbazones have also been proposed by Zuman[9].

(R-C₆H₄)-N=C(SH)-NHNH₂ $\xrightarrow{H^+}$ (R-C₆H₄)-NH-Ċ(SH)-NHNH₂

(R-C₆H₄)-NH-Ċ(SH)-NHNH₂ $\xrightarrow{2e+H^+}$ (R-C₆H₄)-NH-CH(SH)-NHNH₂

Controlled potential electrolysis further suggests 2 electron reduction mechanism for phenylthiosemicarbazide. Four electron reduction mechanism would have resulted in the production of aniline ($-N{=}C- \xrightarrow{4H^+,4e} -NH_2 + -CH_3$). Products were isolated after electrolysis for about 12 hr at 1.6 V in a H shaped cell and did not give any dye test for aromatic amine. Moreover, on analysing the products by tlc and taking aniline as reference, there was no indication of the presence of aniline. This clearly support 2 electron mechanism for the reduction of phenylthiosemicarbazides.

The $E_{1/2}$ was found to shift towards more negative potential with increase in concentration of the depolarizer (Table 1). Such type of change in $E_{1/2}$ values suggests the irreversible nature of the waves. The plots of E_{de} vs $[\log \frac{i}{i_d - i} - 0.546 \log t]$ were found linear. The values of αn and $K^{\circ}_{f,h}$ calculated from the slope and intercept, further suggests the irreversible nature of the waves.

It is observed from Table 2 that the half-wave potentials are shifted towards more negative potential for compounds with substituents having electron donating nature, viz., 2-CH_3, 3-CH_3, 4-CH_3, 2-OCH_3, 3-OCH_3, 4-OCH_3, 2-Cl, 3-Cl, 4-Cl, 2-OC_2H_5, 4-OC_2H_5 and 2,5-$(CH_3)_2$. This behaviour can be accounted for by considering the effect of the substituents. An electron donating group on the benzene ring would increase electron density on carbon attached to the hetero atom, viz. nitrogen due to which the reduction would become less facile and the $E_{1/2}$ would shift to more negative potentials.

Correlation of half-wave potential with Hammett constants : The correlation between the structure of compounds and their chemical reactivity is fundamental problem in organic chemistry. One of the most important and versatile of these correlations is the Hammett equation[10] which relates the effect of structure on the reactivity of the molecule.

For application in polarography, Hammett equation is transformed to the form[11]

$$\Delta E_{1/2} = P + M + S,$$

TABLE 2—POLAROGRAPHIC CHARACTERISTICS OF SOME 4-PHENYLTHIOSEMICARBAZIDES AT pH 10.0 IN 1.0 *M* KCl, CONC. = 0.832 × 10^{-3} *M*

No	R	$-E_{1/2}$, V	i_d, μA	$D_0^{1/2} \times 10^{-6}$	αn	$k^{\circ}_{f,h} \times 10^{-10}$ cm^{-1}	σx
I	H	1.32	1.75	0.32	0 54	1 90	0.00
II	2-CH_3	1.31	1.70	0.30	0 56	1.60	−0.17
III	3-CH_3	1 33	1.70	0.30	0.54	1.70	−0.07
IV	4-CH_3	1.34	1.80	0.38	0.54	1.77	−0.17
V	2-OCH_3	1.32	1.70	0.30	0.57	1 75	−0.39
VI	3-OCH_3	1.33	1.75	0.32	0.54	1.67	−0.11
VII	4-OCH_3	1.35	1.75	0.32	0.56	1.65	−0.27
VIII	2-Cl	1.28	1.80	0.38	0.56	1.65	+0.20
IX	3-Cl	1.29	1.70	0.30	0.57	1.67	+0.37
X	4-Cl	1.30	1.70	0.30	0.54	1.89	+0.23
XI	2-OC_2H_5	1.32	1.80	0.38	0.54	1.86	−0.35
XII	4-OC_2H_5	1.34	1.75	0.32	0.57	1.70	−0.23
XIII	2,5-$(CH_3)_2$	1.30	1.70	0.30	0.59	1.70	−0.24

where P, M and S represent the shift in the half-wave potential due to the change in activation energy by polar, mesomeric and steric effects. In *m*- or *p*-substituted thiosemicarbazides the substituents are rigid and lie much away from the reaction centre with the result that generally the steric interaction between the substituent and reaction centre is almost negligible. The change in $E_{1/2}$ of parent thiosemicarbazide can, therefore, be attributed to the electron repelling nature of the substituent. Thus, when steric effects are not taken into account, the modified Hammett equation,

$$\Delta E_{1/2} = \rho_{\pi}, _R \sigma x,$$

represents the polar effect of the substituents. Considering the relationship for the substituent effect[12]

$$\sigma x = \log k_i - \log k_i^\circ$$

where k_i° and k_i represent the ionisation constants for the unsubstituted and substituted molecules, respectively and σx is the substituent constant. The corresponding relationship for the irreversible wave may be written as

$$\sigma x = \log k^\circ_{f,h_{(sub)}} - \log k^\circ_{f,h_{(unsub)}}$$

The value of σx at *p*H 10.0 thus determined are given in Table 2.

Fig. 2 exhibits the relation between $E_{1/2}$ of substituted thiosemicarbazides and the Hammett substituent constant σx, which include both polar induction and polar configuration effect. It is of interest to note that substituents like 3-Cl, 4-Cl, $3\text{-}CH_3$, $4\text{-}CH_3$, $4\text{-}OCH_3$ and $4\text{-}OC_2H_5$ fit in the straight line, whereas 2-Cl, $2\text{-}CH_3$, $2\text{-}OCH_3$, $2\text{-}OC_2H_5$ and $2,5\text{-}(CH_3)_2$ show deviation. This deviation may be accounted for on the basis of slight steric hindrance to coplanarity. The value of specific rate constant (ρ) was found to be 0.12 V.

Fig 2 Plot of $-E_{1/2}$ vs σ for some 4-phenylthiosemicarbazide in B. R. buffer at *p*H = 10.0.

It is observed in the above reaction series that methyl, chloro, methoxy and ethoxy substituents show positive polarographic *ortho* shift which indicates that *ortho* derivative is easily reducible in comparison to its *p*-analogue.

TABLE 3—POLAROGRAPHIC *ortho* SHIFTS (Δ_0) FOR SOME 4-PHENYLTHIOSEMICARBAZIDES AT *p*H 10.0.

R	Δ_0, V
Methyl	+0.03
Chloro	+0.02
Methoxy	+0.03
Ethoxy	+0.02

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Polarographic Reduction of Some 5,5-Dimethylcyclohexane 2-Benzothiazolylhydrazono-1,3-Diones and its 2-Methyl, 4-Methyl, 4-Methoxy, 4-Ethoxy Derivatives

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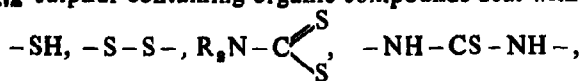
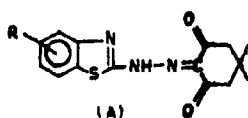
Polarographic studies of some 5,5-dimethylcyclohexane-2-benzothiazolylhydrazono-1,3-diones were carried out in B. R. buffer in the pH range 2.0-12.0. All the compounds gave a single, well defined, irreversible, diffusion controlled reduction wave whose $E_{1/2}$ was pH dependent but i_d remained constant throughout the entire pH range. The $E_{1/2}$ shifted towards negative potential with increase in pH, thereby showing that protonation precedes reduction. The effect of the double layer structure on the $E_{1/2}$ is also studied.

MOST of the polarographic investigations on sulphur containing organic compounds deal with $-SH$, $-S-S-$, $R_2N-C(=S)S$, $-NH-CS-NH-$, $-NH-CS-S-$ and RSO_2H groups[1-4] but not much has been done to study the polarography of other classes of sulphur containing organic compounds such as thiazoles and benzothiazoles[5-7] which are of great biological importance. A knowledge of their redox behaviour at the solution-mercury interface may prove useful from physiological point of view. Moreover, the polarographic behaviour of hydrazones has received little attention[8-9] and little information is available about the hydrazones in which the carbon atom of the $-NH-N=C-$ group is attached to cyclohexane ring. Polarographic studies on the reduction of these compounds at DME were therefore undertaken. The present paper describes the results of such studies on some recently synthesised hydrazono derivatives of 2-aminobenzothiazoles (A).

(A)

Experimental

Apparatus: The polarographic measurements were carried out using a Cambridge pen recording polarograph. The capillary characteristic was 2.040 $mg^{2/3}$ $sec^{-1/2}$. SCE was used as the reference electrode. pH measurements were made with an expanded scale ECIL pH-meter in connection with glass electrodes. The polarograms were recorded at 20±0.1°.

Reagents and solutions: 5,5-Dimethylcyclohexane-2-benzothiazolylhydrazono-1,3-diones having substituents H, 2-CH_3, 4-CH_3, 4-OCH_3 a 4-OC_2H_5, were prepared according to the meth developed earlier[10] and their purity was assu by repeated recrystallisation. Britton-Robin buffers in the pH range 2.0-12.0 were prepared adding requisite amount of 0.2 *M* sodium hyd xide solution to stock acid solution composec boric acid, phosphoric acid and acetic acid. chemicals used were of A. R. grade. Stock sc tion (1×10^{-3} *M*) of hydrazones were preparec dimethylformamide.

Procedure: Solutions for recording pola grams were prepared by mixing 3.0 ml hydraz solution (1.0×10^{-3} *M*), 1.0 ml 1.0 *M* KCl and ml buffer. The polarograms were then recor after passing hydrogen for about 10 min. number of electrons involved in the reduct process were calculated by millicoulom method[11] using $CdSO_4$ solution as reference. controlled potential electrolysis was carried out potential corresponding to the plateau (1.6 V the wave. The electrolysis cell was a H-sha one, the cathodic and anodic compartments be separated by a diaphragm of sintered gl Mercury was used as electrode material. A complete electrolysis (about 6 hr) the catho was analysed for the identification of the product.

Results and Discussion

The compounds listed in Table 1 gave a si 4e reduction wave in B. R. buffer of pH 2.0-1 and in 0.1 *M* NaOH. The nature of the wave found to be diffusion controlled as evident by linear dependence of limiting current on $\sqrt{h}$ concentration of depolarizer. The constancy wave height in the pH range studied, together v the fact that di/dt had a very low value of temp ture coefficient further confirmed that the reduct

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TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF 5,5-DIMETHYLCYCLOHEXANE-2-BENZOTHIAZOLYLHYDRAZONO-1,3-DIONES AT *p*H 7.4 ; CONC. 3.0×10^{-4} *M*

Sl. No.	R	$-E_{1/2}$, V	i_d, μA	I	$\frac{dE_{1/2}}{dpH}$, $\frac{V}{pH}$	$\Delta E_{1/2}$, V	αn I Method*	αn II Method**	P
1	H	0.48	0.85	0.22	0.063	0.00	1.20	1.20	1.22
2	2-CH_3	0.56	0.85	0.22	0.066	0 08	1 02	1.07	1.30
3	4-CH_3	0 51	0.90	0.23	0.062	0.03	1.08	1.10	1.24
4	4-OCH_3	0.51	0.85	0.22	0 062	0.03	1.32	1.28	1.03
5	4-OC_2H_5	0.52	0.85	0.22	0.061	0 04	1.20	1.24	1.11

*Log plots method.
**Oldham and Perry method.

waves were fully diffusion controlled. The wave characteristics are shown in Table 1.

The half-wave potential of these compounds was found to be dependent on *p*H and shifted towards more negative potential with increase in *p*H. The plots of $E_{1/2}$ vs *p*H were linear with slopes in the range 0.061 to 0.066 V/*p*H upto *p*H 8.3 and thereafter there was a small change in $E_{1/2}$. The value of the slope was significantly small. The *irreversible* nature of the waves was confirmed by log plots[12]. The fact that $E_{1/2}$ shifted towards more negative potential with increasing concentration of the depolariser further pointed towards the irreversible nature of the waves. The value of αn_a (product of transfer coefficient and the number of electrons transferred in the rate determining step) and p (number of protons involved during the rate determining step of the reaction) was determined using the expressions[12]

$$E_{1/4}-E_{3/4}=-\frac{0.0517}{\alpha n_a}$$

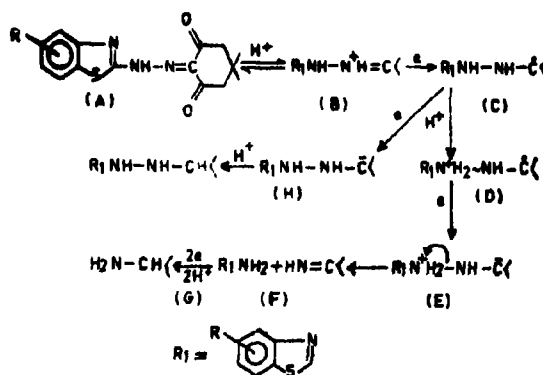
$$\frac{dE_{1/2}}{dpH}=-\frac{0.05915}{\alpha n_a}.p$$

The values of αn_a was also determined by the *method* of Oldham and Perry[13] using the expression

$$E_{1/2}=E_r+\frac{0.0592}{\alpha n_a}\log\left[1.35K_r+\frac{t}{D}\right]$$

where t is the drop time at the potential E_r. The values of half-wave potentials together with $dE_{1/2}/dpH$, αn_a and p are also *given in Table 1*.

Since the $E_{1/2}$ of these thiazoles were *p*H dependent and the limiting current *p*H independent upto *p*H 8.3, *it* was concluded that both *acidic and* basic forms of the compounds reached the electrode surface and are electroactive. Thus, the proton *transfer reaction* precedes the electrode process in such cases. Out of the two general sequences[14] for the proton and electron addition viz., H^+,e, H^+,e and H^+, e, e, H^+, the former sequence was more probable for these compounds in the light of their structural genesis. After the uptake of a proton and one electron the radical (C) would accept a proton to form a protonated *radical (D)* which after taking one electron would get cleaved at nitrogen bond with the formation of aniline. The *imine (F) formed* was further protonated and got reduced.

Alternatively, the radical (C) could also combine with an electron instead of proton but this possibility was cancelled out by the fact that such a reduction would involve only 2 electrons whereas polarographic data clearly indicate 4-electron transfer reactions at the DME.

These mechanistic steps found support from the increase of $E_{1/2}$ with *p*H as protons are consumed in reduction. As the rate of protonation becomes slow the $E_{1/2}$ tends to become constant. Fig. 1

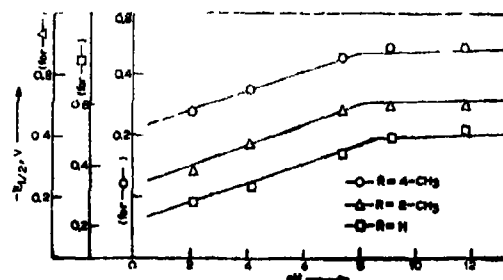
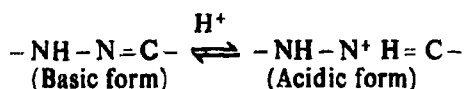



Fig. 1. Plots of $-E_{1/2}$ vs *p*H for some 5,5-dimethylcyclohexane-2-benzothiazolylhydrazono-1,3-diones.

shows that above *p*H 8.3, the shifting of half-wave potential with *p*H towards negative potential is not so marked, as in the acidic range. Moreover, at *p*H above 8.3, *the* $E_{1/2}$ *is practically constant.* In the *p*H range studied where both the electroactive forms (acidic as well as basic) are reduced, half-wave potential of the two forms are so close that the waves merge and no separation is observed.

Similar steps for the reduction of hydrazono group have also been proposed by others[15-17], involving cleavage of the nitrogen-nitrogen bond.

Due to an acid-base equilibrium that exists between two structural forms of the compounds, wave height of the wave remains pH independent as long as the formation of the acidic form from the basic form is fast enough. When pH increases the rate of protonation decreases and the wave height decreases as well.

$$\underset{\text{(Basic form)}}{-NH-N=C-} \overset{H^+}{\rightleftharpoons} \underset{\text{(Acidic form)}}{-NH-N^+H=C-}$$

When the depolariser solution was tested after controlled potential electrolysis, it gave dye test thereby showing that at least one of the reduction product is aromatic amine. UV spectra of the solution during electrolysis were recorded at different intervals of time. λ_{max} CH_3OH at 415 mm for $-NH-N=C-$ grouping showed a decrease in the peak height after each interval of time and finally disappeared, confirming the above reduction mechanism.

Effect of supporting electrolyte concentration : The effect of the double layer structure on the $E_{1/2}$ of a process preceded by the protonation is given by the equation[18],

$$\Delta E_{1/2} \approx \Delta\psi_1 \left(\frac{\alpha n_a - Z}{\alpha n_a} - \frac{\partial E_{1/2}}{\partial pH} \cdot \frac{F}{2.30\,RT}\right) \qquad (1)$$

where ψ_1 is the variation in the double layer potential, α the transfer coefficient, n_a the number of electrons transferred in the rate determining step and Z the charge of the particle being discharged. Undoubtedly, a marked effect of change in ionic strength on $E_{1/2}$ should be observed in cases where the depolarizer is in the ionic form and no such effect should be observed if it is in the non-ionic form, i.e., $Z=0$. Since the second term in the bracket of equation (1) is nearly -1 and $Z=0$, $E_{1/2}$ will be almost independent of ψ_1 or of ionic strength. This was verified by carrying out experiments with varying concentrations of KCl (0.01 *M* to 0.25 *M*). The values of $dE_{1/2}/dpH$ thus obtained fell in the range 60-70 mV/pH and $E_{1/2}$ and i_d remained unaffected by the change in concentration of the supporting electrolyte.

Effect of solvent composition : The polarogram of the above mentioned thiazoles were recorded in the minimum amount of DMF (20%) necessary for the dissolution of the compound. The DMF percentage was then progressively increased from 20 to 60% to see the effect of solvent composition on the electrode process.

$E_{1/2}$ of the compounds was found to shift towards more negative potential almost linearly[19] and that this effect is much more pronounced in compounds having comparatively more positive potential. This shift may be attributed[20] to a decrease in the surface concentration of the electroactive species in addition to a change of pH and pKa of the protonated depolarizer.

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The Reaction of Potassium Permanganate with Potassium Ferrocyanide and Some Binary Mixtures in Presence of Fluoride Ions*

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The reactions of potassium permanganate with potassium ferrocyanide and binary mixtures of ferrous-mercurous (1), ferrocyanide-mercurous (2) and ferrous-ferrocyanide (3) have been studied potentiometrically in acid medium containing fluoride ions. For potassium ferrocyanide, good results are obtained at 0.018-1.8 N H_2SO_4 in presence of 0.238-0.357 M NaF at temperature range 25-50°. But in the case of the mixtures, the optimum acidities are 0.315 N H_2SO_4 (2, 3) and 0.22 N (1) in presence of 0.357 M NaF at 25°. 125-503 mg of ferrocyanide can be determined with high accuracy. The constituents of the mixtures can be titrated in presence of each other. The difficulty of precipitation of manganese(II) ferrocyanide can be overcome by keeping the reduction product of $KMnO_4$ as complex Mn(III) fluoride.

THE reaction between $KMnO_4$ and ferrocyanide in acid medium was studied by De Beer and Hjort[1]. Kolthoff[2] titrated ferrocyanide at concentration less than 0.02 M by comparing the colour at the end point with that of ferrocyanide. Enough acid should be present to prevent the precipitation of manganous ferrocyanide. Potentiometric titration of ferrocyanide in alkaline medium was reported by Issa and Azin[3].

The monovalent mercury[4] and bivalent iron[5] can be titrated quantitatively with $KMnO_4$ in presence of fluoride ions. Ferrous iron reduces $KMnO_4$ under these conditions in two steps with formation of Mn(III) and Mn(II). However, monovalent mercury does not effect the reduction quantitatively to the Mn(II) step. This difference is obviously related to the reducing power of the different species which is known to depend on the redox potential values of the system concerned which amount to 0.92, 0.771 and 0.36 volt, respectively[6]. It is therefore of interest to find out how binary mixtures of these species and ferrocyanide behave in their oxidation with $KMnO_4$.

Experimental

Potassium permanganate, potassium ferrocyanide, mercurous nitrate and ferrous sulphate solutions were prepared from chemically pure salts and standardised according to recommended procedures. 4.5 M H_2SO_4 and 0.476 M NaF were also prepared from chemically pure products. The titration equipment is the same as described earlier[7].

Results and Discussion

Reaction between potassium permanganate and potassium ferrocyanide :

The titration curves of ferrocyanide with $KMnO_4$ in absence of F^- ions and acidity of 0.045 M H_2SO_4 includes one inflection corresponding to the reduction of $KMnO_4$ to Mn(II). This inflection amounts to 230 mV per 0.05 ml of the titrant. In presence of NaF of different molarities (0.119-0.357 M) a second inflection appears, representing the oxidation of the originally produced Mn(II) to Mn(III). Under these conditions the second end point coincides with the theoretical value in presence of NaF (0.238 to 0.357 M) and occurs somewhat earlier at 0.119 M NaF. The first inflection occurs about 14% earlier than expected on the basis of the formation of Mn(II). This is obviously due to partial precipitation of ferrocyanide as the Mn(II) salt. However, this precipitate undergoes oxidation at the second step together with the initially formed Mn(II). This fact finds support from the effect of acidity on the titration process. As the acidity of the solution is increased the first end point retreats slowly until it coincides with the theoretical value for the Mn(II) step at 0.45 M H_2SO_4. The second end point always coincides with that expected for the Mn(III) step. At higher acidities (0.675 M) the second inflection disappears and the curve is restricted to the first step.

At temperatures between 25-40 and at an acidity of 0.02 M, the two inflections do not deviate from the theoretical values. At 50° the Mn(II) step approaches the theoretical values probably as a result of the increased solubility of the Mn(II) ferrocyanide. The second end point is attained earlier than the expected value due to the partial decomposition of $KMnO_4$ at high temperature.

Titration of different quantities of ferrocyanide can be achieved when the second end point is taken into consideration. The first end point shows larger negative errors on increasing the concentration of ferrocyanide. The amount of ferrocyanide precipitated apparently increases with the increase

* This work was carried out under the supervision of the late Prof. I. M. Issa.

in the concentrations of the reactants—Mn(II) and ferrocyanide.

The redox potentials of the ferric/ferrocyanide couple and that of Mn(III)/Mn(II) couple under various conditions were evaluated from the titration curves (Figs. 1 and 2). The data in Table 1 indicate an increase of the formal potential with rise of acidity and decrease of fluoride ion concentration. They are not affected much by temperature or concentration of the reactants.
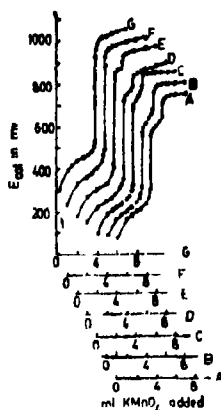
Fig. 1. Titration of 0.00842 N $K_4[Fe(CN)_6]$ with 0.0922 N $KMnO_4$ in presence of NaF (0.357 M) and H_2SO_4 of different molarities.

A – 0.009 M, B – 0.0225 M, C – 0.045 M, D – 0.225 M, E – 0.45 M, F – 0.675 M and G – 0.90 M H_2SO_4.

Titration of a mixture containing Fe(II) and Hg_2^{2+}:

The titration curve of this mixture (Fig. 3) is characterised by two inflections, the first of which is small and amounts to 25-35 mV. The second inflection is larger and amounts to 170-230 mV. The first step corresponds to the oxidation of
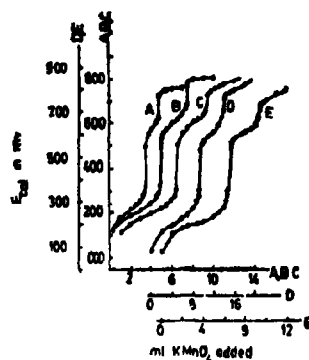
Fig. 2. Titration of different molarities of $K_4[Fe(CN)_6]$ with 0.0922 N $KMnO_4$ at optimum conditions.

A – 0.00842 N, B – 0.00547 N, C – 0.00684 N, D – 0.0108 N and E – 0.0137 N $K_4[Fe(CN)_6]$.
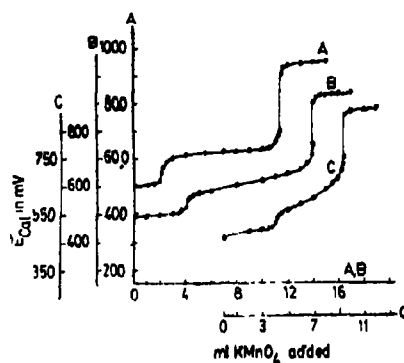
Fig 3 Titration of a mixture containing Fe^{2+} and Hg_2^{2+} with 0.0922 N $KMnO_4$ in presence of 0.225 N H_2SO_4 and 0.357 N NaF.

A – 0.000828 N Fe^{2+} and 0.006528 N Hg_2^{2+}, B – 0.001656 N Fe^{2+} and 0.006528 N Hg_2^{2+} and C – 0.001656 N Fe^{2+} and 0.008264 N Hg_2^{2+}.

TABLE 1—TITRATION OF $K_4[Fe(CN)_6]$ WITH 0.0922N $KMnO_4$ IN PRESENCE OF 0.357 M NaF AT 25°

$K_4[Fe(CN)_6]$		Volume of $KMnO_4$ consumed (ml)		Theoretical end point (ml)		Error		Inflection at end point (mV/0.05 ml)		Formal redox potential (V)	
ml	mg	a	b	a	b	a	b	a	b	1	2
5	125	3.51	4.65	3.75	4.69	–6.41	–0.85	112	88	0.474	0.824
8	201	4.92	7.50	6.02	7.51	–18.10	–0.13	130	74	0.476	0.842
10	251	6.50	9.35	7.50	9.38	–13.33	–0.32	146	58	0.449	0.842
15	377	9.41	13.96	11.23	14.07	–16.21	–0.78	152	46	0.469	0.848
20	503	13.00	18.60	15.01	18.76	–13.40	–0.85	158	29	0.464	0.852
Acidity ml	M										
0.2	0.009	3.41	4.68	3.75	4.69	–9.10	–0.21	176	70	0.450	0.844
0.5	0.0225	3.56	4.67	3.75	4.69	–5.33	–0.42	218	68	0.453	0.862
1.0	0.045	3.61	4.65	3.75	4.69	–3.73	–0.84	308	32	0.475	0.973
5	0.135	3.65	4.65	3.75	4.69	–2.67	–0.84	312	20	0.498	0.994
10	0.225	3.75	4.63	3.75	4.69	nil	–1.26	377	18	0.550	1.108
15	0.45	3.75	—	3.75	4.69	nil	—	395	—	0.614	—
20	0.9	3.72	—	3.75	4.69	–0.80	—	400	—	0.688	—

Normality of $KMnO_4$ on the basis of valency change $Mn^{7+} \longrightarrow Mn^{2+}$.
(a) $MnO_4^- \longrightarrow Mn^{3+}$; (b) $Mn^{3+} \longrightarrow Mn^{2+}$.
(1) $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system, (2) Mn^{3+}/Mn^{2+} system.

ferrous iron since the formal redox potential depicted from this step amounts to about 617 mV which is in harmony with the values obtained in the titration of ferrous iron alone[6]. The end point, as is evident from Table 2, is attained when $KMnO_4$ is reduced to the Mn(II) step.

The second inflection in the titration curve represents oxidation of mercurous mercury and the formed manganese(II) whereby MnO_4^- is reduced to Mn(III). The redox potential value, as evaluated from the second inflection, amounts to about 900 mV which approximates that of the Hg^{2+}/Hg_2^{2+} couple under the prevailing experimental conditions. The second end point coincides fairly well with theoretical values based on complete oxidation of Fe(II) and Hg(I) whereby MnO_4^- is reduced to the manganic state. The separation of the two steps of reduction is in harmony with the apparent difference in the redox potential of the two systems involved in the reaction. The success of the titration is confirmed by varying the amounts of the two reductants in the mixture and also by titrating the separate constituents alone under the same experimental conditions. The results depicted in Table 2 are in harmony with these speculation.

Titration of a mixture containing ferrocyanide and mercurous mercury :

The curves obtained in the titration of this mixture are approximately similar to those obtained in the case of ferrous iron and mercurous mercury and obviously represent the same sequence of the reaction steps (Fig. 4). The first inflection represents oxidation of ferrocyanide whereby MnO_4^- is reduced to Mn(II). The latter, together with monovalent mercury, is oxidised in the second step whereby MnO_4^- is reduced to Mn(III). The occurrence of these two steps is in harmony with the redox potential values of the systems involved, which amount to 0.432 and 0.93 V for the $[Fe(CH)_6]^{3-}/[Fe(CN)_6]^{4-}$ and the Hg^{2+} systems, respectively. The end points (Table 3) coincide fairly well with the theoretical values for the
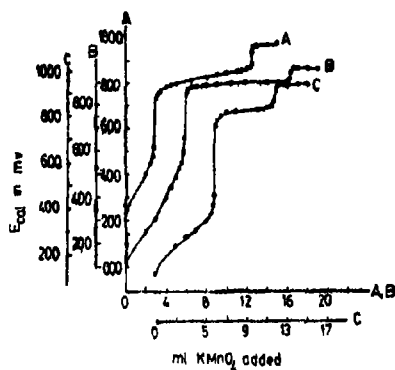
Fig. 4. Titration of a mixture of 0.0684 $N\,[Fe(CN)_6]^{4-}$ and 0.0816 $N\,Hg_2^{2+}$ in presence of 0.815 $N\,H_2SO_4$ and 0.357 N NaF.

A – 0.002736 $N\,[Fe(CN)_6]^{4-}$ and 0.006528 $N\,Hg_2^{2+}$,
B – 0.00546 $N\,[Fe(CN)_6]^{4-}$ and 0.006528 $N\,Hg_2^{2+}$ and
C – 0.00543 $N\,[Fe(CN)_6]^{4-}$ and 0.003264 $N\,Hg_2^{2+}$.

different mixtures titrated. The mechanism of the reaction is confirmed by comparing the titration curve of the mixture with the titration curves of the separate constituents.

Titration of a mixture containing ferrous iron and potassium ferrocyanide :

The titration curves of this mixtures (Fig. 5) show two inflections. The first step as gathered from the redox potential of the two systems involved amounting to 150 and 260 mV, respectively, indicates oxidation of ferrocyanide whereby MnO_4^- is reduced to Mn(II). The inflection involves oxidation of both ferrous iron and the manganous manganese produced in the first step. These speculations are confirmed by the coincidence of the end point with the theoretical and comparison of the curves of the mixture with those of the separate constituents. The data in Table 4 are in conformity with these facts.

Contrary to expectations, ferrous iron did not produce a step corresponding to the reduction of

TABLE 2—TITRATION OF 0.0457 $N\,Fe^{2+}$ SOLUTION AND 0.0816 $N\,Hg_2^{2+}$ SOLUTION WITH 0.0922 $N\,KMnO_4$ IN PRESENCE OF 0.357 M NaF

Mixture	H_2SO_4 9 N (ml)	Theoretical end point (ml)				Exp. end point (ml)		Error %		Max. inflec (mV/ 0.05 ml)		Formal redox potential (V)	
		Fe^{2+}		Hg_2^{2+}		1st	2nd	1st	2nd	1st	2nd	Fe^{3+}/Fe^{2+}	Mn^{3+}/Mn^{2+}
		Mn^{2+}	Mn^{3+}	Mn^{2+}	Mn^{3+}	Inflection		Inflection		Inflection		system	system
4 ml Fe^{2+}	2.5	2.06	2.57	7.08	8 85	2.07	11.45	+0.48*	+0 26**	23	190	0.747	0 864
8 ml Hg_2^{2+}	10 0	2.06	2.57	7.08	8.85	2.05	11 89	−0.48	−0.26	22	195	0 802	0.939
8 ml Fe^{2+}	2.5	4.12	5.14	7.08	8 85	4.10	18.95	−0.24	−0.28	30	175	0 788	0.850
8 ml Hg_2^{2+}	10.0	4.12	5.14	7 08	8 85	4.09	18 93	−0.78	−0.43	28	230	0.742	0.877
8 ml Fe^{2+}	2.5	4.12	5.14	3.54	4.34	4.10	9.56	−0.49	+0 84	28	170	0.722	0.837
4 ml Hg_2^{2+}	10.0	4.12	5.14	3.54	4.31	4.08	9.55	−0.97	+0.74	35	180	0.707	0.903
8 ml Fe^{2+}	2.5	4.12	5.14	–	–	4.10	5.12	−0.24	−0.39	310	25	0.617	1.264
8 ml Hg_2^{2+}	2.5	–	–	7.08	8.85	—	8.89	–	−0.45	–	205	–	0.930§

*Mn^{2+}/Fe^{3+} **Mn^{3+} (total) § Hg(II)/Hg(I) system

TABLE 3—TITRATION OF MIXTURES OF 0.068 N $[Fe(CN)_6]^{4-}$ AND 0.0816 N Hg_2^{2+} WITH 0.0922 N $KMnO_4$ IN PRESENCE OF 0.857M NaF

Mixture	H_2SO_4 9 N (ml)	Theoretical end point (ml) $[Fe(CN)_6]^{4-}$ Mn^{2+}	$[Fe(CN)_6]^{4-}$ Mn^{3+}	Hg_2^{2+} Mn^{2+}	Hg_2^{2+} Mn^{3+}	Exp. end point (ml) 1st Inflection	2nd Inflection	Error % 1st Inflection	2nd Inflection	Max. inflec. mV/0.05 ml 1st Inflection	2nd Inflection	F. redox potential (V) $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$	Mn^{3+}/Mn^{2+}
4 ml $[Fe(CN)_6]^{4-}$	2.5	3.0	3.78	7.08	8.85	2.98	12.60	−0.67*	−0.24**	170	50	0.604	1.070
+8 ml Hg_2^{2+}	10	,,	,,	,,	,,	3.98	12.52	+0.67	−0.87	70	28	0.782	1.182
8 ml $[Fe(CN)_6]^{4-}$	2.5	6.02	7.51	,,	,,	5.99	16.4	−0.49	−0.36	162	32	0.550	1.144
+8 ml Hg_2^{2+}	10	,,	,,	,,	,,	5.97	16.34	−0.88	−0.78	205	88	0.502	1.070
8 ml $[Fe(CN)_6]^{4-}$	2.5	,,	,,	3.56	4.45	5.96	11.87	−0.99	+0.75	220	30	0.517	1.072
+4 ml Hg_2^{2+}	10	,,	,,	,,	,,	6.01	11.98	−0.16	+0.17	218	28	0.546	1.045
8 ml $[Fe(CN)_6]^{4-}$	2.5	6.02	7.51	—	—	6.08	7.54	+0.16	+0.40	325	38	0.482	1.006
8 ml Hg_2^{2+}	2.5	—	—	7.08	8.85	—	8.91	—	+0.68	—	205	—	0.930§

* Mn^{3+}/Fe^{3+} ** Mn^{3+} (total) § Hg(II)/Hg(I) system

TABLE 4—TITRATION OF MIXTURE OF 0.0684 N $[Fe(CN)_6]^{4-}$ AND 0.0457 N Fe^{2+} WITH 0.0922 N $KMnO_4$ IN PRESENCE OF 0.857 M NaF

Mixture	H_2SO_4 9 N (ml)	Theoretical end point (ml) $FeSO_4$ Mn^{2+}	$FeSO_4$ Mn^{3+}	$[Fe(CN)_6]^{4-}$ Mn^{2+}	$[Fe(CN)_6]^{4-}$ Mn^{3+}	Exp. end point (ml) 1st Inflection	2nd Inflection	Error % 1st Inflection	2nd Inflection	Inflection mV/0.05 ml 1st	2nd	F. redox potential (V) $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$	Mn^{3+}/Mn^{2+}
4 ml Fe^{2+} +	0.5	2.06	2.57	6.02	7.51	5.97*	10.0**	−0.85	−0.70	150	30	0.436	1.01
8 ml $[Fe(CN)_6]^{4-}$	3.5	2.06	2.57	6.02	7.51	6.00	10.05	−0.34	−0.29	220	40	0.457	1.076
8 ml Fe^{2+} +	0.5	4.12	5.15	6.02	7.51	5.99	12.6	−0.51	−0.47	238	45	0.432	1.019
8 ml $[Fe(CN)_6]^{4-}$	3.5	4.12	5.15	6.02	7.51	6.0	12.55	−0.34	−0.87	255	40	0.446	1.067
8 ml Fe^{2+} +	0.5	4.12	5.15	3.0	3.78	3.02	8.90	−0.67	−0.34	260	85	0.388	1.034
4 ml $[Fe(CN)_6]^{4-}$	3.5	4.12	5.15	3.0	3.78	3.01	8.89	−0.33	−0.45	375	30	0.445	1.082
8 ml Fe^{2+} +	0.5	4.12	5.15	6.02	7.51	6.0	12.6	−0.34	−0.48	287	40	0.397	0.998
8 ml $[Fe(CN)_6]^{4-}$	1.0	4.12	5.15	6.02	7.51	5.99	12.58	−0.51	−0.64	239	38	0.417	1.007
	2.5	4.12	5.15	6.02	7.51	6.0	12.56	−0.34	−0.80	240	40	0.418	1.044
	5.0	4.12	5.15	6.02	7.51	5.97	12.55	−0.85	−0.88	240	38	0.427	1.107
	10.0	4.12	5.15	6.02	7.51	5.98	12.53	−0.68	−1.04	242	36	0.467	1.129
8 ml $[Fe(CN)_6]^{4-}$	0.5	—	—	6.02	7.51	6.01	7.50	−0.17	−0.13	295	30	0.482	1.109
8 ml Fe^{2+}	0.5	4.12	5.15	—	—	4.09	5.12	−0.72	−0.58	310	25	0.612§	1.252

*$Mn^{3+}/[Fe(CN)_6]^{4-}$ **Mn^{3+} (total) §Fe(III)/Fe(II) system
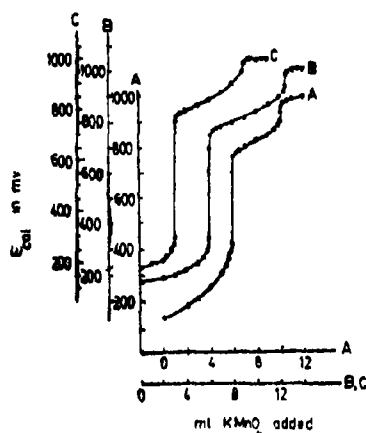
Fig. 5. Titration of 0.0684 N $[Fe(CN)_6]^{4-}$ and 0.0457 N Fe^{2+} with 0.0922 N $KMnO_4$ in presence of 0.815 N H_2SO_4 and 0.857 N NaF.

A – 0.000828 N Fe^{2+} and 0.00543 N $[Fe(CN)_6]^{4-}$,
B – 0.001656 N Fe^{2+} and 0.00543 N $[Fe(CN)_6]^{4-}$ and
C – 0.001656 N Fe^{2+} and 0.00273 N $[Fe(CN)_6]^{4-}$.

MnO_4^- to Mn(II) state as occurs with pure ferrous solution, inspite of the relatively low potential of the Fe(III)/Fe(II) system. The potential corresponding to the second step amounts to 1 volt, a value very close to that of the Mn(III)/Mn(II) couple. The absence of a step corresponding to Fe(III)/Fe(II) system can be explained by the interaction of the formed ferricyanide with the ferrous iron present to form Turnbull's blue. The latter apparently undergoes oxidation at a relatively higher potential than that of the ferric/ferrous system.

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Methylation of Phenol over Alumina in the Vapour Phase : Influence of Copper Sulphate

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Phenol is methylated using methanol over alumina and alumina impregnated with varying amounts of copper sulphate at 360, 400 and 440°, at a molar ratio of 0.75 : 1 of phenol to methanol. Over alumina, phenol undergoes direct nuclear (carbon) methylation, giving cresols and xylenols. Alumina with 10 and 20% copper sulphate catalyses both carbon and oxygen methylation forming cresols and anisole, respectively. Xylenols, which were absent over the above two catalysts, appear when the copper sulphate concentration increases to 30%. Further increase of copper sulphate from 30 to 40% not only enhances the proportion of xylenols in the products by increasing the temperature and the contact time, but also decreases that of anisole under these conditions. However, the concentration of cresols seems to be unaffected. Methylation of phenol follows a first order kinetics irrespective of the concentration of copper sulphate in the catalysts.

ALKYLATION is an important unit process widely employed in chemical industries for introducing alkyl groups into other substances notably in hydrocarbons and hydroxy compounds of the aromatic series. Among the alkylation reactions, methylation of phenol has got great industrial importance, as methyl phenols are largely used as chemical intermediates for the production of valuable industrial products. Most of the work done on methylation of phenol is patented[1-3]. Consequently, very little information regarding these investigations is available. Others, who studied this reaction, used high acidic alumina[4-6], zeolite[7] and silica-alumina[8], with a view to get more of *m*-cresol, probably on account of its importance as a raw material for perfumes. Kotanigawa[9-11] and co-workers investigated extensively the methylation of phenol using Fe_2O_3 catalyst impregnated with various metallic oxides and observed that Fe_2O_3-CuO was the most effective combination for selective methylation of phenol at the *ortho* position to get 2,6-xylenol. It has been reported recently[12] that alumina doped with copper sulphate suppresses the formation of xylenols and the product composition consists of a mixture of anisole and cresols. In the present investigation, alumina-copper sulphate has been employed to study the methylation of phenol in detail and to obtain the kinetic parameters.

Experimental

Preparation of materials :

Alumina A : Alumina was prepared by hydrolysing aluminium isopropoxide (B.D.H., A.R.) with distilled water. The precipitated aluminium hydroxide was filtered, washed thoroughly, cut into cakes, dried at 120° for 24 hr and activated at 500° in a stream of dry air for another 24 hr. The activated samples were sieved (85-120 mesh) and a part of it was mixed with 0.5% analytical grade stearic acid binder and made into cylindrical pellets of 0.5 cm diam and 4 mm height and the rest was used as support for copper sulphate.

Catalysts B, C, D and E were obtained by impregnating alumina A with appropriate amounts of copper sulphate (B.D.H., A.R.) solution in water to give respectively 10, 20, 30 and 40% by weight of copper sulphate. Catalysts B, C, D and E were made into pellets of the same size mentioned above. Prior to each run the catalyst was kept at 500° for 8 hr in an atmosphere of pure dry oxygen until no oxides of carbon was detected in the exit gas. After use, it was found that the copper sulphate remained unaffected.

Phenol used was of B.D.H., AnalaR grade and used as such. Methanol (B.D.H., L.R.) was purified further by fractionation. The purity of reactants was checked by gas chromatography.

Apparatus and procedure :

The reactions were carried out at atmospheric pressure in a fixed bed flow type reactor. The experimental set-up is shown in Fig. 1, which consists of (i) a constant flow bottle, (ii) preheater-vapourizer, (iii) a capillary flow meter for metering the feed, (iv) tubular reactor and (v) condenser and receiver.

The mixed feed was passed through a capillary tube flow meter which was calibrated earlier using the actual reactant mixtures. The feed enters the preheater-vapourizer (15 cm long and 1.2 cm internal diam) maintained at 220° through a micro feeder for conversion into vapour before entering the reactor. The catalyst (6.36 g) was kept in a Pyrex glass reactor tube (1.5 cm internal diam and 20 cm long). Pyrex glass beads (4 mm diam) were placed above the catalyst bed to a height of 3 cm. A vertical

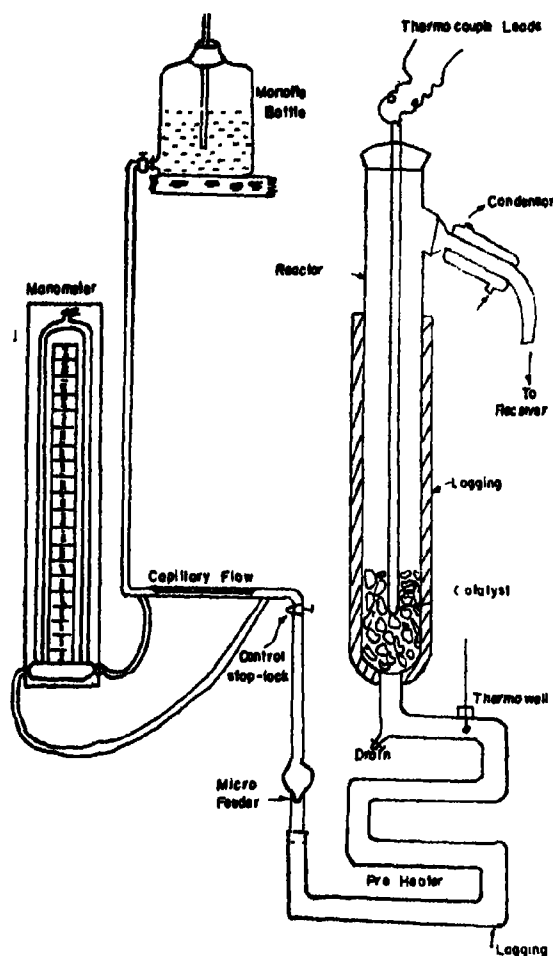



Fig. 1. Experimental set-up

thermowell is provided for inserting thermocouple to measure the temperature of the catalyst bed. The reaction products were passed through a condenser and collected in a receiver kept in ice. Both the preheater and the reactor were heated on the outside by a uniformly wound nichrome wire, whose length had been predetermined to give the requisite temperature. This was then lagged by means of asbestos cords and magnesia powder to prevent loss of heat. The energy input is controlled by a 8 A dimmerstat. The temperature of the catalyst bed is indicated by a Pt-Pt-Rh thermocouple connected to a temperature controller-cum-indicator.

The liquid products collected for the first 15 min of each run of 45 min duration were discarded, and the products collected after this period were analysed. This was done to ensure the attainment of steady state for the reaction over the catalyst, and also to eliminate temperature fluctuations, if any, due to the starting of the reaction. The catalyst was regenerated after the reaction. Runs were repeated to check the reproducibility of the results.

The liquid products of methylation of phenol were identified and estimated using a one meter column of Apiezon-L in a gas chromatograph (Model NCL-AIMIL MK II B) with Flame Ionization Detector. The optimum condition for the best resolution within a reasonable time was found to be : column temperature 130°, FID temperature 225°, nitrogen inlet pressure of 15 psi with hydrogen as fuel.

For the identification of different peaks in a chromatogram, retention times for the different compounds were obtained by introducing pure substances. For quantitative estimation, synthetic mixtures containing the different compounds in varying known proportions were introduced and calibration curves relating the concentration with peak area were drawn[13-15].

Results and Discussion

The thermodynamic feasibility of methylation of phenol to cresols had been ascertained by calculating the free energy change of the reaction by Van Krevelan's method using the equation,

$$F_T = A + BT$$

where A and B are constants of the equation. Using standard values[16] for the constants A and B, the change in free energy for the reaction at 600, 650 and 700°K were calculated and the values are found to be −17.37, −17.33 and −17.07 kcal/mole, respectively, indicating that methylation of phenol is quite feasible within the temperature range given above. Three contact times, namely, 17.05, 23.44 and 37.50 hr were chosen by trial and error methods. The reactions were carried out at 360, 400 and 440° and the molar ratio of phenol to methanol was kept constant at 0.75 : 1 throughout the investigation. The above temperatures were chosen because the conversion was found to be low below 360° and the phenols may decompose to benzene, toluene and xylene above 440°.

Increase of both contact time (Table 1 ; Fig. 2) and temperature (Table 2 ; Fig. 3) enhances the conversion of phenol over each catalyst but the enhancement is found not to be linear. The concentration of alkyl phenols in the product increased

Table 1—Effect of Contact Time on Product Distribution in Moles at 400°

Catalyst	Contact time in hr	Anisole formed	Cresol formed	Xylenol formed	Phenol unreacted
	17.05	—	0.6230	0.1642	0.2128
A	23.44	—	0.7414	0.1880	0.0706
	37.50	—	0.7268	0.1446	0.1291
	17.05	0.4995	0.3715	—	0.1290
B	23.44	0.5010	0.3800	—	0.1190
	37.50	0.4982	0.3990	—	0.1028
	17.05	0.3211	0.5881	—	0.0876
C	23.44	0.3210	0.5900	—	0.0890
	37.50	0.3185	0.6118	—	0.0697
	17.05	0.2020	0.6380	—	0.1600
D	23.44	0.2180	0.6400	—	0.1420
	37.50	0.2100	0.6580	0.0520	0.0800
	17.05	0.0400	0.5828	0.2502	0.1275
E	23.44	0.0458	0.5900	0.2760	0.0887
	37.50	0.0524	0.6100	0.2800	0.0576

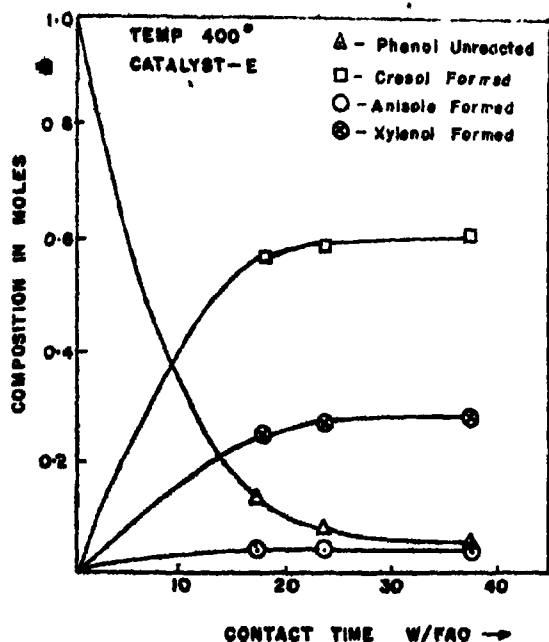



Fig. 2. Effect of contact time on product distribution at 400° over catalyst E.

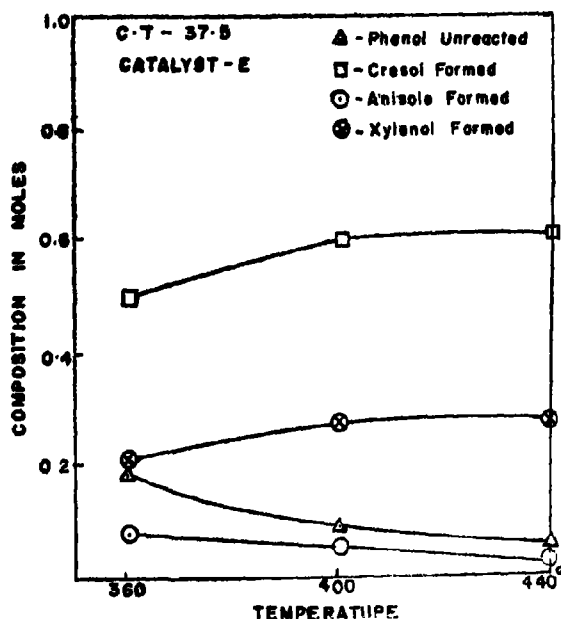



Fig. 3. Effect of temperature on product distribution at a contact time of 37.5 hr over catalyst E.

with increase of these two parameters over each catalyst while the proportion of anisole went down under these conditions. The effect of copper sulphate on the distribution of products depended mainly on its concentration in the catalyst (Tables 1 and 2 ; Fig. 4).

Over alumina (catalyst A), anisole was absent, cresols were formed to a maximum extent of 0.74 mole per mole of phenol reacted along with a sizable amount of xylenols. The absence of anisole

TABLE 2—EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION IN MOLES AT CONTACT TIME 37.5 HR.

Catalyst	Temp °C	Anisole formed	Cresol formed	Xylenol formed	Phenol unreacted
A	360	—	0.5264	0.0698	0.4088
	400	—	0.7263	0.1446	0.1291
	440	—	—	—	—
B	360	0 4523	0.3911	—	0.1566
	400	0 4983	0.3990	—	0.1028
	440	0 4012	0 4607	0.0520	0.0960
C	360	0.3018	0.5014	—	0.1968
	400	0.3185	0.6118	—	0.0697
	440	0.2612	0 6531	0.0580	0.0277
D	360	0.2016	0 6053	0.0488	0.1448
	400	0 2100	0 6580	0 0520	0.0800
	440	0 1200	0 7604	0.0985	0.0211
E	360	0.0821	0 5000	0 2099	0.1980
	400	0 0524	0.6100	0.2800	0.0576
	440	0.0256	0.6100	0.2800	0.0844

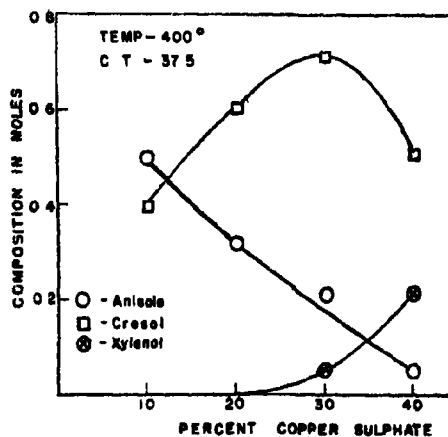



Fig. 4 Effect of copper sulphate on product distribution. Temp. 400°, contact time 37.5 hr.

over this catalyst may be attributed to either (i) direct nuclear methylation of phenol or (ii) rearrangement of anisole, that may be formed, by simultaneous parallel reactions as indicated in the reaction scheme. The complete absence of anisole in the product rules out its formation and subsequent rearrangement to alkyl phenols though this type of rearrangement was observed by Cullaine and Chard[17] over alumina. It may be concluded that over alumina, direct nuclear methylation of phenol occurs.

Impregnation of alumina with 10% copper sulphate (catalyst B) brings about the following changes in the activity pattern of the catalyst. Over this catalyst, anisole is formed to a maximum extent of 0.5 mole while the amount of cresols are reduced considerably with complete elimination of xylenols. The same type of products are formed over catalyst C and also over catalyst D except at high temperature and high contact time (*vide* Tables 1 and 2). In the case of catalyst E, a considerable proportion of xylenols is formed in addition to anisole and cresols.

Unlike over catalyst A, both oxygen and carbon methylations occur simultaneously over catalysts B

to E giving anisole and cresols as suggested in the scheme. With increase in reaction temperature, contact time and copper sulphate concentration in the catalyst, the anisole rearranges to cresols which are further methylated to xylenols, and as a result, C/O ratio increases. The rearrangement of anisole to cresol was confirmed by injecting anisole through catalyst E. The various possible transformations are given in the scheme.

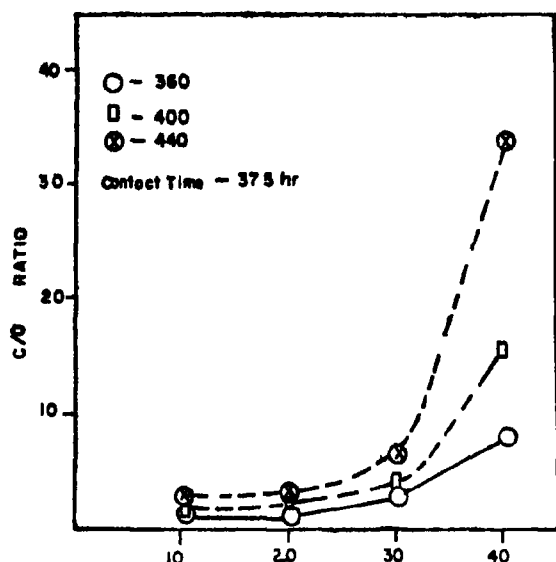



Fig. 5. Effect of copper sulphate on C/O ratio at three temperature. Contact time 37.5 hr.

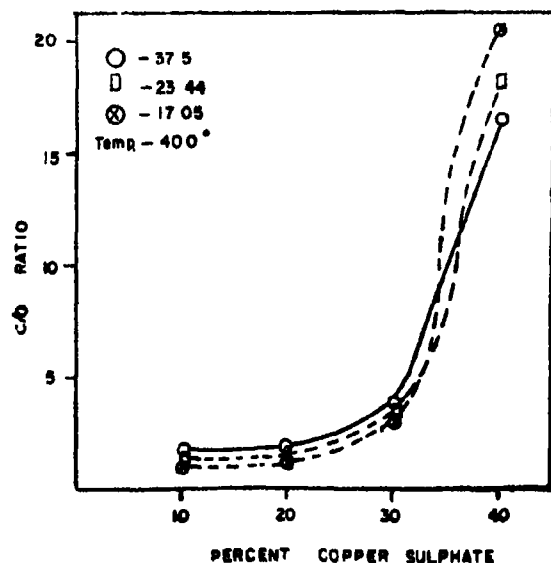



Fig. 6. Effect of copper sulphate on C/O ratio at three contact times. Temp. 400°.

Though the observed data over alumina-copper sulphate agree partly with the report appearing in a chemical weekly[18] that copper sulphate when incorporated with alumina gives a product composition consisting of anisole and cresols, they do not agree with the observation that copper sulphate suppresses the formation of xylenols. It may be emphasised that not only the proportion of xylenols in the product increases with increase in copper sulphate concentration, the anisole concentration is also reduced drastically (*vide* Tables 1 and 2).

Kinetics : The reaction sequence pertaining to the methylation of phenol, illustrated in the reaction scheme, shows that it involves parallel and consecutive steps simultaneously thereby making the process complex. On account of the complexity of the reaction, the kinetics of the reactant alone is followed by its disappearance with time. A plot of $-\ln(1-x)$, (where x is the mole of phenol reacted) vs contact time (i.e., W/F_{A_0}, where W is the weight of the catalyst and F_{A_0} is the flow rate of the reactant mixture/hr) for catalyst E shows a straight line relationship (Fig. 7) indicating that the methylation of phenol follows a first order kinetics. The

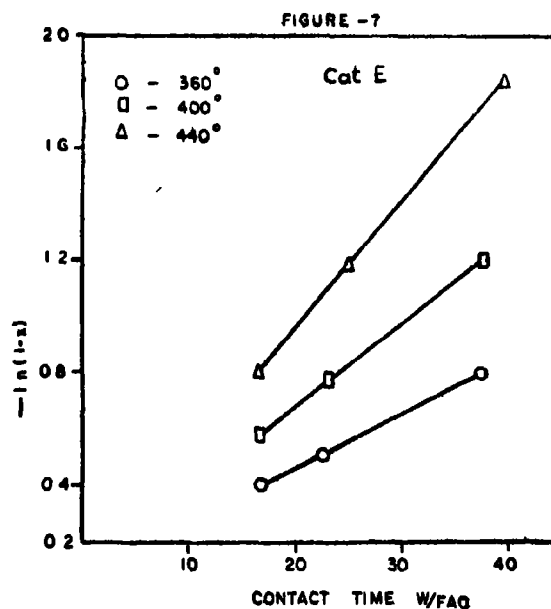



Fig 7. First order plot for catalyst E.

TABLE 3—EFFECT OF TEMPERATURE ON C/O RATIO (CARBON METHYLATION / OXYGEN METHYLATION)

Catalyst	Temp. °C	C/O ratio 17.05 hr	C/O ratio 23.44 hr	C/O ratio 37.50 hr
	360	1.0060	0.9594	0.8649
B	400	0.7488	0.7588	0.8010
	440	1.0800	1.1050	1.2528
	360	1.6000	1.6440	1.6600
C	400	1.8000	1.8880	1.9200
	440	2.6000	2.6000	2.7180
	360	8.0500	2.9900	8.2440
D	400	8.2700	8.2100	8.6800
	440	7.8400	10.2700	7.1560
	360	5.5100	8.1500	8.7700
E	400	20.5500	18.8100	16.4800
	440	56.0000	68.7600	84.7500

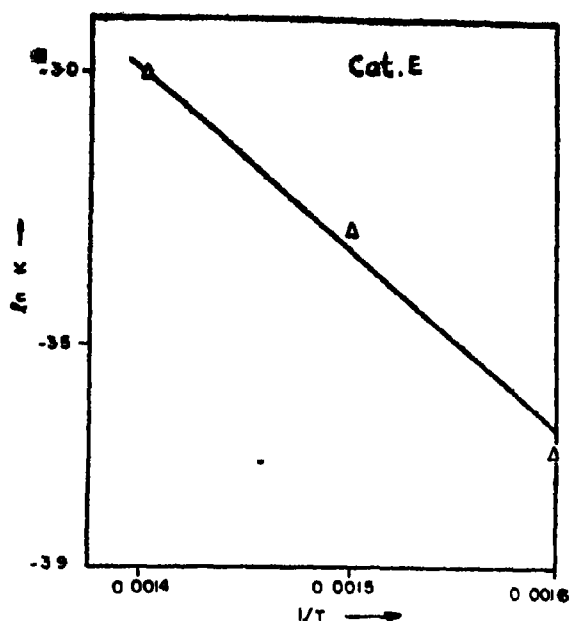



Fig. 8. Arrhenius plot for catalyst E.

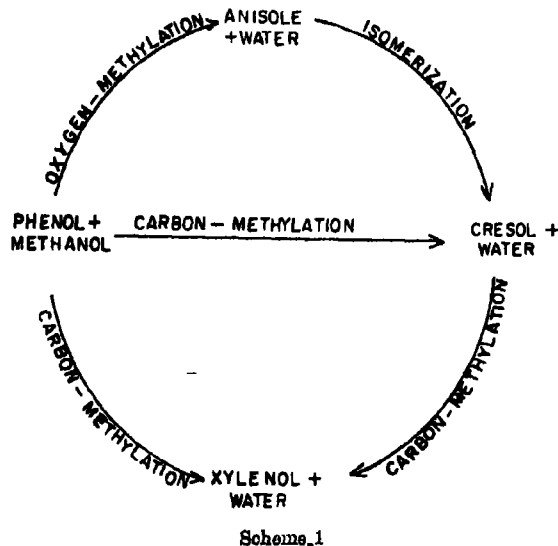
Scheme 1

log of rate constants was plotted against the reciprocal of absolute temperature for catalyst E (Fig. 8). The activation energies, calculated from the slopes of the Arrhenius plots of all the catalysts, are shown in Table 4.

TABLE 4—EVALUATION OF REACTION RATE CONSTANTS

Catalyst	Rate constant k (hr^{-1})			Energy of activation kcal/mole
	k_{360}	k_{400}	k_{440}	
A	—	—	—	7.60
B	0.0095	0.0125	0 0180	7 20
C	0 0120	0.0170	0.0240	6.98
D	0.0160	0.0270	0.0340	6.60
E	0.0220	0.0340	0.0520	6.40

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Studies in Fluorinated 1,3-Diketones and Related Compounds. Part—XIV : Search for New NMR Shift Reagents

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New fluorinated europium 1,3-diketonates have been synthesised and characterized by ir, ^{1}H-nmr and ^{19}F-nmr spectral studies as possible nmr shift reagents and the shifts produced with *n*-hexanol, *n*-heptanol, *p*-fluoroaniline and *m*-trifluoromethylaniline have been studied.

^{1}H-NMR spectra of simple organic molecules are not complicated as the resonances do not overlap at easily accessible field strengths but in the spectra of complex molecules, many resonances do overlap and important structural information may be lost.

Hinckley[1], in 1969, reported the potential of rare earth chelates as nmr shift reagents and described the successful applications of lanthanide shift reagents to a wide range of structural problems. Horrocks[2] tested several $Ln(thd)_3$ reagents, some of which caused still greater shifts than the classical Eu and Pr chelates.

A number of similar reagents, e.g. *tris* (dibenzoylmethanate) and *tris* (benzoylacetonates), were also reported but did not appear to offer any particular advantage over the dipivaloylmethanates. Subsequently, Feibush *et al*[3] reported fluorinated lanthanide shift reagents. These reagents proved to be superior to their non-fluorinated analogues as they provide improved solubility due to perfluoroalkyl groups and the presence of fluorine atoms on the ligands confers higher Lewis acidity on the lanthanide. This higher acidity makes it a more versatile shift reagent for general applications.

Our recent interest in the chemistry of fluorinated 1,3-diketones prompted us to examine some new fluorinated 1,3-diketonatoeuropium chelates as possible nmr shift reagents and thus add to the variety of useful lanthanide shift reagents. For this purpose, we have selected [4,4,5,5,6,6,6-heptafluoro-1-(4′-fluorophenyl)-1,3-hexanedionato]europium(III) $[(hfh)_3Eu]$ and [4,4,5,5,5-pentafluoro-1-(4′-fluorophenyl)-1,3-pentanedionato] europium(III) $[(pfp)_3Eu]$, synthesized by us earlier[4], as possible nmr shift reagents and have studied the shifts produced with *n*-hexanol, *n*-heptanol, *p*-fluoroaniline and *m*-trifluoromethylaniline using a 60 MHz spectrometer model RB-12.

TABLE 1—SHIFT STUDIES OF *n*-HEXANOL, *n*-HEPTANOL, *p*-FLUOROANILINE, *m*-TRIFLUOROMETHYLANILINE BY $Eu(pfp)_3$ AND $Eu(hfh)_3$ IN $CDCl_3$ (1 ml)

Sl. No.	Shift reagent	Nucleophile	Ratio of Shift Reagent : Nucleophile (in mg)	Time in hr	Position of different signals in δ ppm					
					$-OH$	$-CH_2$ attached to OH	$(CH_2)_5/(CH_2)_4$	CH_3	$-NH_2$	$-$Aromatic protons
1.	$Eu(pfp)_3$	*n*-heptanol	Control	1	4.25	3.55	1.4	0.9		
2.	$Eu(pfp)_3$	*n*-heptanol	6 : 1	2	3.5	3.60	1.3	0.85		
3.	$Eu(pfp)_3$	*n*-heptanol	6 : 1	3.5	3.7	3.65	1.35	0.9		
4.	$Eu(pfp)_3$	*n*-heptanol	6 : 1	24	3.9	3.65	1.35	0.9		
5.	$Eu(pfp)_3$	*n*-hexanol	Control	1	4.45	3.55	1.4	0.9		
6.	$Eu(pfp)_3$	*n*-hexanol	5 : 1	2	4.0	4.2	1.4	0.9		
7.	$Eu(pfp)_3$	*n*-hexanol	5 : 1	24	3.9	4.0	1.3	0.85		
8.	$Eu(hfh)_3$	*n*-heptanol	Control	1	4.25	3.55	1.4	0.9		
9.	$Eu(hfh)_3$	*n*-heptanol	6 : 1	1.5	4.15	3.5	1.25	0.85		
10.	$Eu(hfh)_3$	*n*-heptanol	3 : 1	2	4.35	3.45	1.20	0.75		
11.	$Eu(hfh)_3$	*n*-heptanol	2 : 1	70	4.65	3.6	1.35	0.95		
12.	$Eu(hfh)_3$	*n*-hexanol	Control	1	4.45	3.55	1.4	0.9		
13.	$Eu(hfh)_3$	*n*-hexanol	5 : 1	2.5	3.15	3.5	1.3	0.85		
14.	$Eu(hfh)_3$	*n*-hexanol	5 : 1	60	3.45	3.5	1.3	0.85		
15.	$Eu(pfp)_3$	*p*-fluoroaniline	Control	1					3.5	6.3-7.0
16.	$Eu(pfp)_3$	*p*-fluoroaniline	3 : 1	1					5.9	6.6-7.2
17.	$Eu(pfp)_3$	*m*-trifluoromethylaniline	Control	1					3.65	6.2-7.3
18.	$Eu(pfp)_3$	" "	4 : 1	1					5.15	6.9-7.5
19.	$Eu(pfp)_3$	" "	2 : 1	1.5					5.0	6.9-7.4
20.	$Eu(pfp)_3$	" "	2 : 1	48					5.15	6.9-7.4

Experimental

Synthesis of polyfluorinated 1,3-diketones : These polyfluorinated 1,3-diketones have already been reported by us[4,5].

Europium 1,3-diketonates : $EuCl_3$ (0.004 mole), dissolved in a minimal amount of methanol, was added dropwise to a methanolic solution of β-diketonatoenolate anion (0.012 mole). The complex was precipitated by slow addition of water to the resulting methanolic solution. The precipitated europium 1,3-diketonates were crystallized from benzene and dried in vacuum, over phosphorus pentaoxide, for 24 hr[6].

Results and Discussion

The substrate associates with the complex at the hydroxyl group (*n*-hexanol, *n*-heptanol) or the amino group (*p*-fluoroaniline or *m*-trifluoromethylaniline) and the induced shifts decrease rapidly with increasing distance of protons from the hydroxyl group. The results are tabulated in Table 1.

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Synthesis of Some New Benzimidazoles as Antiamoebic Agents

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Fourteen new substituted 1′-acetyl [3N-aminomethyl substituted quinazolono]-2′-alkyl substituted phthalamido benzimidazoles have been synthesised and their effect on the axenic culture of *Entamoeba histolytica* have been studied *in vitro* at 125 μg/ml. Some of them have shown significant antiamoebic activity.

THE discovery and success of metronidazole (2-methyl-5-nitro-1-ethanol imidazole) as a potent amoebicidal agent stimulated research in imidazole chemistry. A number of compounds of this category have been synthesised and tested for various therapeutic effects[1-3]. Some nitro imidazoles[4-7] have been shown to possess marked amoebicidal and trichomonacidal activity. A lot of work has also been done with the benzimidazole moiety as benzimidazoles have shown significant antibacterial, antiviral and antifungal activity[8,9]. This prompted us to synthesise some substituted benzimidazoles and screen them for amoebicidal activity.

Experimental

Melting points of the compounds synthesised were determined in open capillary tubes. Infrared spectra were taken on a Perkin-Elmer 157 spectrophotometer in KBr pellets. NMR spectra were taken on Perkin-Elmer model R32 at a frequency of 90 MHz. TLC was carried out by using silica-gel coated glass plates of 2 mm thickness, using benzene-methanol (10 : 1) as the solvent.

Infrared spectra : The infrared spectra of the compounds in Tables 1, 2 and 3 show sharp peaks at 3000-3400 cm^{-1} (–NH), 1700 cm^{-1} ($-\overset{\displaystyle O}{\overset{\|}{C}}-NH$) and 1500 cm^{-1} ($-NO_2$).

NMR spectra ($DMSOd_6$) *:* These benzimidazoles gave a singlet at δ 2.26 for $N-CH_2-N$, singlet at δ 4.28 for $N-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}$ and multiplet between δ 6.24-δ 8.38 for the aromatic protons.

The identity of the compounds was further confirmed by their melting points and elemental analysis, while the purity was ascertained by thin layer chromatography.

2-Alkyl substituted benzimidazoles : These were prepared by the method of Cescon and Day[10].

3-Nitro phthalic anhydride : This was synthesised by the method given in Vogel[11].

Substituted 3-N-aminomethyl 4(3H)quinazolones : The method of Mukerji and Nautiyal[12] was followed for the synthesis of these quinazolones.

2-[Phthalamido-alkyl]-benzimidazoles (a) *:* 2-Alkyl-substituted benzimidazole (0.01 mole), 3-nitro phthalic anhydride (0.01 mole) and dry pyridine (7 ml) were refluxed together for 5-6 hr on a sand bath. The reaction mixture, after cooling, was poured into ice-cold water containing a few drops of conc. HCl. The precipitate was filtered, washed with cold water, dried and crystallised from ethanol.

Four new 2-[phthalamido-alkyl]-benzimidazoles were thus synthesised (Table 1).

TABLE—1

Sl No	R	R_2	m.p. °C	Molecular formula
1	CH_2	H	242	$C_{16}H_{11}N_3O_2$
2	CH_2CH_2	H	264(d)	$C_{17}H_{13}N_3O_2$
3.	CH_2	3-NO_2	>275	$C_{16}H_{10}N_4O_4$
4	CH_2CH_2	3-NO_2	242	$C_{17}H_{12}N_4O_4$

Yield ranged between 55-60%

%N within ± 0.3% of the theoretical values.

3-[N-(Chloroacetyl)-aminomethyl]4(3H)quinazolones (b) *:* To substituted 3-N-aminomethyl 4(3H)quinazolone (0.01 mole)[12], chloroacetyl chloride (0.01 mole) was added and the mixture refluxed for 2-2½ hr in presence of dry benzene (12 ml). The flask was cooled, excess benzene distilled off, the solid filtered, washed with ice-cold water, dried and recrystallised from methanol.

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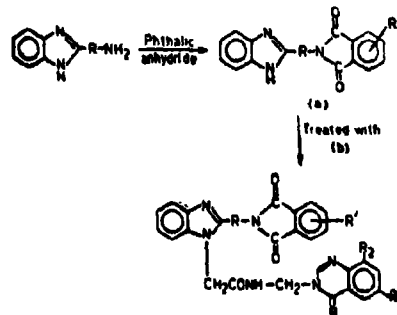
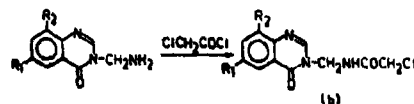
Four such compounds were prepared (Table 2).

TABLE—2

Sl. No.	R_1	R_2	m.p. °C	Molecular formula
1.	H	H	244	$C_{11}H_{10}N_3O_2Cl.2HCl$
2.	Br	H	268	$C_{11}H_9N_3O_2ClBr.2HCl$
3.	Br	Br	270(d)	$C_{11}H_8N_3O_2ClBr_2.2HCl$
4.	NO_2	H	265(d)	$C_{11}H_9N_4O_4Cl.2HCl$

Yield ranged between 65-70%.
% N within ± 0.4% of the theoretical values.
Isolated as hydrochlorides.

Substituted 3-[N-(1'-acetyl)-aminomethyl]quinazolono-2'-[phthalamido-alkyl] benzimidazoles : An equimolar mixture of (a) and (b) was refluxed in dry acetone (12 ml) in presence of anhydrous potassium carbonate (0.015 mole) for 3-4 hr. Excess acetone was distilled off and methanol added to the solid residue. The mixture was heated till the reactants dissolved leaving the potassium carbonate behind. Excess methanol was distilled off, the solution cooled and the solid after filtration and drying was recrystallised from methanol. Fourteen such compounds were synthesised (Table 3).

Scheme

Pharmacology :

For the evaluation of amoebicidal activity of the compounds, the method of Das *et al*[18] was followed, except for the TPS-1 medium which was kept at *p*H 6.8 and not 7.2, since acidic *p*H is favourable for growth of the amoebae.

A three day old culture of *E. histolytica* was used and the final results were obtained after observing under an inverted microscope after 72 hr. Amoebicidal activity was carried out at 125 µg/ml. Out of the fourteen compounds screened, three were

TABLE—3

Sl. No.	R	R'	R_1	R_2	m.p °C	Molecular formula	Amoebicidal activity at 125 µg/ml
1.	CH_2	H	H	H	>275	$C_{27}H_{20}N_6O_4.2HCl$	NA
2.	CH_2	H	Br	H	220(d)	$C_{27}H_{19}N_6O_4Br.2HCl$	NA
3.	CH_2	H	Br	Br	>275	$C_{27}H_{18}N_6O_4Br_2.2HCl$	NA
4*.	CH_2	H	NO_2	H	270(d)	$C_{27}H_{19}N_7O_6.2HCl$	125
5.	CH_2CH_2	H	H	H	>275	$C_{28}H_{22}N_6O_4.2HCl$	NA
6.	CH_2CH_2	H	Br	H	200(d)	$C_{28}H_{21}N_6O_4Br.2HCl$	NA
7.	CH_2CH_2	H	Br	Br	180(d)	$C_{28}H_{20}N_6O_4Br_2.2HCl$	NA
8.	CH_2CH_2	H	NO_2	H	>275	$C_{28}H_{21}N_7O_6.2HCl$	NA
9.	CH_2	$3-NO_2$	H	H	>275	$C_{27}H_{19}N_7O_6.2HCl$	NA
10.	CH_2	$3-NO_2$	Br	H	285(d)	$C_{27}H_{18}N_7O_6Br.2HCl$	NA
11.	CH_2	$3-NO_2$	Br	Br	273(d)	$C_{27}H_{17}N_7O_6Br_2.2HCl$	NA
12*.	CH_2	$3-NO_2$	NO_2	H	270(d)	$C_{27}H_{18}N_8O_8.2HCl$	125
13*.	CH_2CH_2	$3-NO_2$	H	H	273(d)	$C_{28}H_{21}N_7O_6.2HCl$	125
14.	CH_2CH_2	$3-NO_2$	Br	Br	>275	$C_{28}H_{19}N_7O_6Br_2.2HCl$	NA

Yield ranged between 45-50%.
C, H, N ranged within ± 0.4% of the theoretical values.
The compounds were isolated as hydrochlorides.
*Amoebicidal at 125 µg/ml.
NA=Non-amoebicidal.

active at this concentration. Emetine hydrochloride and metronidazole (FLAGYL) were used as the standard drugs, the former was active as 62.5 µg/ml and the latter at 7.8 µg/ml at *p*H 6.8.

Results and Discussion

The results of the bioassay show that three compounds are active at 125 µg/ml. All the three compounds, i.e. no. 4, no. 12 and no. 13 (Table 3) have a nitro group either in the quinazolone moiety or in the phthalamido ring. The presence of a bromo group in the quinazolone ring system has not been effective in exhibiting the amoebicidal activity in these compounds. Therefore, the only conclusion that can be drawn from these results is that the nitro group, irrespective of its position is responsible for activity in the compounds.

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Synthesis of α-Aminoadipic Acid

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A two-step synthesis of α-aminoadipic acid in quite encouraging yield through reduction and hydrolysis of azlactone of succinic anhydride with hydriodic acid in presence of red phosphorus has been reported.

SEVERAL synthetic schemes for the preparation of α-aminoadipic acid have been reviewed by Greenstein and Winitz[1]. Published methods show that only the azlactones of acetic and phthalic anhydrides have been used for the synthesis of amino acids. Attenburrow and co-workers[2] prepared threonine from 2-phenyl-4-(1-hydroxyethylidene)-5-oxazolone, an azlactone of acetic anhydride. Recently[3], we have employed 2-phenyl-4-phthalidene-5-oxazolone for the synthesis of β-amino-β-(*o*-benzene carboxylic acid) alanine. We now describe the formation of 2-phenyl-4-succinylidene-5-oxazolone and α-aminoadipic acid from this azlactone.

Unlike the analogous preparation of azlactones of carbonyl compounds, reaction of succinic anhydride (1) with hippuric acid (2) gives some other products in addition to the azlactone. Treatment of the anhydride (1) with hippuric acid (2) in presence of fused sodium acetate as a base catalyst and acetic anhydride affords 2-phenyl-4-succinylidene-5-oxazolone (3) as well as benzoic acid (4) and N-acetylglycine (5). This is due to the transformation of hippuric acid into benzoic acid and glycine to some extent by water produced during the course of azlactone formation in the reaction mixture. The liberated glycine reacts with acetic anhydride to yield N-acetylglycine (5). If in this reaction, the sodium acetate is replaced by triethylamine, the rate of hydrolysis is increased and the compounds (4) and (5) are formed in excess.

Condensation of glycine with equimolecular proportion of succinic anhydride in presence of acetic anhydride and fused sodium acetate results in the formation N-acetylglycine (5) and water soluble pigments, when the mixture is warmed for various lengths of time. The compound (5) does not react with succinic anhydride to give 2-methyl-4-succinylidene-5-oxazolone, an analogue of the product (3). If excess of glycine is taken keeping other reaction conditions the same, polymerization takes place and a green fluorescing polymer is obtained.

Subjection of the compound (3) to hydrolysis with hydroiodic acid in presence of red phosphorus and glacial acetic acid leads to simultaneous scission of the lactone and oxazolone rings as well as the benzoyl group. The carbon-carbon double bond is also reduced during the hydrolysis. No difficulty is encountered in the isolation of the amino acid (6) from the reaction mixture. After hydrolysis is complete, which takes 2 *hr*, the contents are filtered and the filtrate is evaporated to dryness under reduced pressure after trituration with solvent ether. In this way the salt of α-aminoadipic acid is obtained which on treatment with ammonia gives the free amino acid (6) in a well crystallized form (Fig. 1).

Experimental

Synthesis of 2-phenyl-4-succinylidene-5-oxazolone (3) : An intimate mixture of succinic anhydride (10 g), hippuric acid (17.9 g) and fused sodium acetate (8.4 g) was heated with acetic anhydride (30 ml) on an electric hot plate to obtain a clear solution and then on a steam bath for 2 hr. The reaction mixture was poured in ice-cold water. The gummy product separated was extracted with sodium carbonate solution to remove benzoic acid and then with light petroleum ether (40-60°). The azlactone was obtained on evaporation of the ether. This was purified by a column of alumina using benzene ; m.p. 114-15°, yield 4.19 g (16%). Anal. Found : C, 64.49 ; H, 3.70 ; N, 5.48. Calcd. for $C_{13}H_{9}NO_{4}$; C, 64.20 ; H, 3.73 ; N, 5.76%.

The water layer obtained from the above reaction mixture was evaporated to dryness and the residue was dissolved in methanol. On cooling, crystallized product, *N-acetylglycine* (5), was obtained. This was filtered and dried, m.p. 205-6°, mixed m.p. 205°. Anal. Found : C, 40.79 ; H, 6.31 ; N, 12.23. Calcd. for $C_{4}H_{7}NO_{3}$; C, 41.02 ; H, 6.03 ; N, 11.96%.

Synthesis of α-aminoadipic acid (6) : 2-Phenyl-4-succinylidene-5-oxazolone (2 g) was refluxed with

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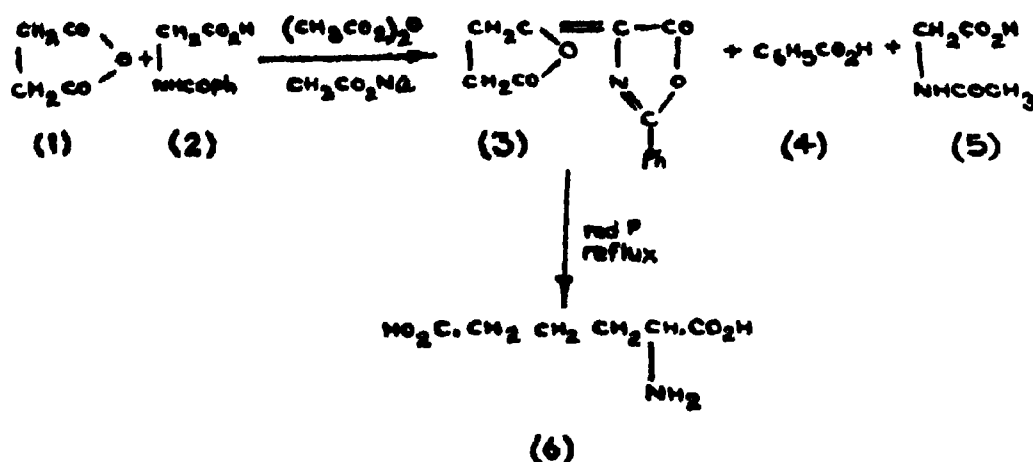
Fig. 1

a mixture of hydriodic acid[1] (sp. gr. 1.7 ; 15 ml), glacial acetic acid (10 ml) and red phosphorus (2.5 g) for 2 hr. Unreacted phosphorus was filtered and the filtrate was evaporated to dryness under diminished pressure. The residue was taken up in 20 ml of water and re-evaporated. The residue was again suspended in water (25 ml) and extracted several times with ether to remove benzoic acid. The aqueous layer was neutralized carefully with ammonia solution. The separated amino acid (6) was filtered, washed with ethanol and dried ; m.p. 204-5° (lit.[4,5] m.p. 206° and 202°), yield 0.88 g (95%). IR(KBr) 3020, 1900, 1650, 1580, 1500, 1250, 1180 and 760 cm^{-1}. Anal. Found: C, 44.52 ; H, 7.08 ; N, 8.91. Calcd. for $C_6H_{11}NO_4$; C, 44.71 ; H, 6.88 ; N, 8.69%.

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High Content of Cholesterol in the Lipid of *Acacia farnesiana* Leaves**

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The lipidic composition of the leaves of *Acacia farnesiana* has been determined using gas liquid chromatographic techniques. The light petroleum extract has been found to contain *n*-alkanes ($C_{21}-C_{33}$) with maximum occurrence of *n*-nonacosane (60%), triacontanol and phytosterols : cholesterol (8.7%), campesterol (21.6%), stigmasterol (37.2%) and sitosterol (32.4%). Occurrence of this relatively large amount of cholesterol (8.7%) in plants is an unique finding.

ACACIA farnesiana commonly called 'Vilayati kikar' in Hindi belongs to family "Mimosaceae". The plant is cosmopolitan in tropics. According to *Sushruta's* "Kaharagoda", the plant is one of the ingredients in a preparation for the treatment of snake bite[1]. The tender leaves, bruished in a little water, are swallowed for treatment of gonorrhoea. Only β-diketones and flavones have been isolated from some Acacia species[2]. The oil of *Acacia farnesiana* has been analysed by Demole[3]. Considering its medicinal importance and the fact that no systematic work on the leaves of this species has been done so far, a chemical analysis of the leaves was undertaken.

TABLE 1—COMPOSITION OF *n*-ALKANES

Sl. No	*n*-Alkanes		Composition⁺ %
1.	*n*-henicosane	$C_{21}H_{44}$	0.2
2.	*n*-docosane	$C_{22}H_{46}$	0.6
3	*n*-tricosane	$C_{23}H_{48}$	0.6
4.	*n*-tetracosane	$C_{24}H_{50}$	0 7
5	*n*-pentacosane	$C_{25}H_{52}$	2.5
6	*n*-hexacosane	$C_{26}H_{54}$	2.7
7	*n*-heptacosane	$C_{27}H_{56}$	18.0
8.	*n*-octacosane	$C_{28}H_{58}$	11.6
9	*n*-nonacosane	$C_{29}H_{60}$	60.0
10	*n*-triacontane	$C_{30}H_{62}$	1.8
11	*n*-hentriacontane	$C_{31}H_{64}$	1.2
12	*n*-dotriacontane	$C_{32}H_{66}$	0 5
13.	*n*-tritriacontane	$C_{33}H_{68}$	traces

⁺ According to glc analysis.

Experimental

The leaves of *Acacia farnesiana* were collected locally. Air dried leaves (600 g) were extracted thrice with light petroleum (60-80°) at boiling temperature for 36 hr. A dark green solid (4%) was obtained. It was found to be neutral and gave positive Libermann-Burchard test. After usual work-up, the extract was chromatographed over a column of neutral activated alumina (~20 fold excess) and gave different fractions on elution with increasing polarity of the solvent.

Fraction A : Elution with hexane and crystallisation from acetone gave a waxy product (22 mg), m.p. 59-61°. It gave a single spot on tlc (silica gel plate impregnated with 2% $AgNO_3$). IR spectrum indicated it to be a long chain aliphatic hydrocarbon. GLC analysis represented the homologous series of *n*-alkanes ($C_{21}-C_{33}$) with maximum occurrence of *n*-nonacosane (C_{29} ; 60.0%) and *n*-heptacosane (C_{27} ; 18.0%). Odd numbered homologues predominated only in the higher members (Table 1). Some branched hydrocarbons were also present in traces. The distribution pattern of *n*-alkanes has been found to be of unimodal type[4].

Fraction B : Further elution of the column with petroleum ether : benzene (1 : 4 v/v) gave another waxy product, homogeneous on tlc. It was crystallised from methanol (1.754 g), m.p. 85-86°. Its ir spectrum indicated it to be a long chain primary aliphatic alcohol showing prominent peaks at 1060, 3360 cm^{-1}. It was characterised as *n*-triacontanol on the above basis and on comparison with authentic specimen (co-tlc and m.m.p.). Its acetyl derivative[5] had m.p. 68-69° and was identical with the authentic derivative (co-tlc and m.m.p.).

Fraction C : The next fraction of sterol was obtained on elution with benzene : chloroform (3 : 1). It gave positive Libermann-Burchard test and yellow colour with tetranitromethane. This fraction, on crystallisation from methanol, gave shining crystals (130 mg), m.p. 138-40°. This fraction was then acetylated (m.p. 131-32°) in Ac_2O-pyridine and the identification of each sterol was carried out as the acetates by argentation tlc followed by glc on both OV-1 and OV-17 SCOT glass capillary column. The acetylated sterol mixture was separated into three different zones by argentation tlc having R_f value of the least polar

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zone 0.87 (zone 1) and the medium polar zone 0.80 (zone 2) while the most polar zone (zone 3) was not evident.

The fraction from zone 1 was a mixture of cholesterol, campesterol and sitosterol. The next fraction from zone 2 consisted mainly of the acetate of stigmasterol. The fraction from zone 3 was shown to contain the acetates of cholesterol, campesterol, sitosterol and stigmasterol which might have resulted from the "tailing" of the components on the argentation tlc. The approximate content of each of the four sterols in the acetylated total sterol fraction as determined by glc on OV-1 column, has been given in Table 2.

TABLE 2—COMPOSITION OF STEROLS

Sterol acetate	OV-1(%)	RRT* OV-1	RRT* OV-17
Cholesterol	8 7	1 00	1 00
Campesterol	21 6	1 29	1 32
Stigmasterol	37 2	1 41	1.44
Sitosterol	32 4	1 61	1 64

* Retention times of cholesterol acetate 7 93 has been taken to be 1.00.

It is worth mentioning here that the occurrence of relatively larger amount of cholesterol (8.7%) in this plant is an unique finding. Cholesterol is generally of animal origin, but is widely distribute in higher plants in trace amount[6].

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Amperometric Estimation of La^{3+} and Ce^{3+} with Cupferron using d.m e.

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Cupferron has been employed as a reagent for the amperometric titrations of La^{3+} and Ce^{3+} in very dilute solution using d.m.e. Hydrochloric acid ($pH=2.75$) has been used as supporting electrolyte. These titrations revealed cupferron to metal ratio of 1 : 1. Titrations are not hampered by the presence of a fairly large amount of Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Cl^{-}, Br^{-}, I^{-}, NO_3^{-}, NO_2^{-}, CH_3COO^{-} and ClO_4^{-} ions. Furthermore, micro and ultramicro quantities of La^{3+} and Ce^{3+} have been successfully determined with an error of less than ±0.70%.

CUPFERRON, an ammonium salt of N-nitroso-phenyl hydroxylamine [$C_6H_5N(NO)ONH_4$] was introduced as a precipitant for Cu^{2+} and Fe^{3+}. The reagent has been successfully used in the determination of metals, such as those belonging to titanium family[1]. Kolthoff and Liberti[2] have amperometrically titrated Cu^{2+} ion with cupferron using d.m.e. as an indicator electrode. The amperometric titration of yttrium and some other rare earths using a rotating platinum anode and stationary platinum cathode in an ammoniacal acetate medium of pH 3.5 to 6, has been reported by Vasilenko[3]. The use of cupferron in the amperometric titrimetry of various other ions e.g. Fe^{3+}, Tl^{3+}, Sn^{4+}, Pr^{3+} and Nd^{3+} has been discussed in the literature. No account, however, is available in literature on the use of cupferron as a reagent for amperometric titration of La^{3+} and Ce^{3+} on a d.m.e.

The results of amperometric titrations of La^{3+} and Ce^{3+} with cupferron on a d.m.e. at $pH = 2.75 \pm 0.01$ are reported in the present paper.

Experimental

Cupferron (B.D.H.) was purified[8] by recrystallisation from ethanol. The dried crystals were stored in dark over ammonium carbonate. A fresh solution of this reagent was prepared in air free distilled water before use and the solution was standardised by amperometric titration method[8]. La^{3+} and Ce^{3+} solutions were prepared by dissolving a calculated amount of $La(NO_3)_3 \cdot 6H_2O$ [Riedel] and $CeCl_3 \cdot 6H_2O$ [Fluka], respectively in the required volume of double distilled water. The solutions were standardised by conventional titrimetric method[9].

Hydrochloric acid (pH=2.75) was used as a supporting electrolyte for the study of the polarographic behaviour of cupferron and purified nitrogen gas was passed through the solutions before recording the polarograms. A manul polarographic set up with multiflex galvanometer (sens = 8.10×10^{-9} amp/div) was used for measurement o current. The d.m.e. used in conjunction with S.C.E had the characteristics m = 2.45 mg/sec, t = 2.5 sec drop and h = 43.5 cm.

For titrations, a number of solutions containin calculated amounts of La^{3+} and Ce^{3+} (0.005 mM to 0.05 mM) were prepared. The pH of thes solutions was adjusted at 2.75 with hydrochlori acid. Titrations of these solutions were carrie out at an applied voltage of − 1.20 volts (vs S.C.E. using an H-type cell with d.m.e. as an indicato electrode and S.C.E. as reference electrode.

Results and Discussion

Cupferron gives a well defined cathodic wave i hydrochloric acid[10]. The half wave potentia varies with pH. The height of the diffusion curren is proportional to the concentration of cupferro The plateau potential of the polarogram for cup ferron, i.e. − 1 20V (vs S.C.E.) (at which La^{3+} or Ce^{3} do not give any diffusion current) was applied. Th metal ion solution in dil. HCl (pH = 2.75) was take in a titration cell and the solution was titrate against cupferron (pH = 2.75). After each additio of an aliquot of the titrant the galvanometer readin was noted. On plotting galvanometer readin against the titrant volume a reversed L shape curve was observed (Fig 1). The end point ha been located graphically as the point of intersectio of the two straight lines. This estimates the meta to cupferron ratio of 1 : 1 (Tables 1 and 2). Th literature, however, records 1 : 3 stoichiometri ratio of metal (La^{3+} or Ce^{3+}) to cupferron. Th observed 1 : 1 ratio may be attributed to th relatively low pH value of the test solution[7,11].

Similar results were observed by choosing meta as titrant and the rare earth as titrate under th identical experimental conditions. In this case a L shaped curve was observed.
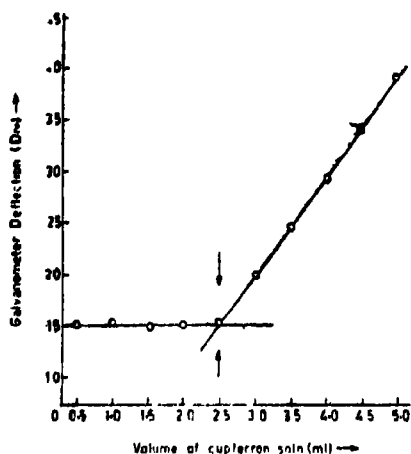
TABLE 1—AMPEROMETRIC DETERMINATION OF La^{3+} WITH CUPFERRON

pH=2.75 ± 0.01

Amount of La^{3+} taken (m*M*)	Amount of Cupferron consumed (m*M*)	Mole ratio M : L	% error
0.005	0.005	1 : 1	—
0.010	0.010	1 : 1	—
0.015	0.0149	1 : 0.993	- 0.70
0.020	0.020	1 : 1	—
0.025	0.0249	1 : 0.996	- 0.40
0.030	0.0298	1 : 0.993	- 0.70
0.040	0.0401	1 : 1.0025	+ 0.25
0.050	0.05	1 : 1	—

TABLE 2—AMPEROMETRIC DETERMINATION OF Ce^{3+} WITH CUPFERRON, pH=2.75 ± 0.01

Amount of La^{3+} taken (m*M*)	Amount of Cupferron consumed (m*M*)	Mole ratio M : L	% error
0.005	0.00503	1 : 1.0060	+ 0.60
0.010	0.010	1 : 1	—
0.015	0.01492	1 : 0.9946	- 0.54
0.020	0.0201	1 : 0.9950	- 0.50
0.025	0.025	1 : 1	—
0.030	0.0302	1 : 1.0067	+ 0.67
0.040	0.040	1 : 1	—
0.050	0.0502	1 : 1.004	+ 0.40

The data in Tables 1 and 2 clearly indicate that the method is successfully applicable for the estimation of micro and ultramicro quantities of the metal ions under study with an error of less than ±0.70%.

Effect of diverse ions : Concentrated solutions of the diverse ions used were prepared. For interference studies, known amount of diverse ion was added to a definite amount of metal ion and the pH was adjusted to 2.75 using dil HCl solution. The solution was titrated against cupferron amperometrically as described above. Titrations are not in any way hampered by the presence of different amount of the diverse ions (Table 3). Moreover,

TABLE 3—EFFECT OF DIVERSE IONS ON THE AMPEROMETRIC DETERMINATION OF La^{3+} AND Ce^{3+}

Metal taken : La^{3+}=0.01 m*M*(1.3891 mg), Ce^{3+}=0.01 m*M*(1.4012 mg)

Diverse ion added	La^{3+} found (mg)	% error	Ce^{3+} found (mg)	% error
K^{+}(180 mg)	1.3920	+ 0.20	1.3937	- 0.53
Na^{+}(115 mg)	1.3781	- 0.79	1.4086	+ 0.53
Al^{3+}(67 mg)	1.3854	- 0.26	1.3929	- 0.59
Mg^{2+}(60 mg)	1.3782	- 0.78	1.4106	+ 0.67
Li^{+}(35 mg)	1.4015	+ 0.89	1.3950	- 0.44
Zn^{2+}(16 mg)	1.3804	- 0.62	1.4185	+ 1.23
Cr^{3+}(7 mg)	1.4058	+ 1.20	1.3851	- 1.15

Figures within parenthesis indicate the maximum amount of foreign ion which do not interfere under the experimental condition

a fairly large amount of the ions Cl^-, I^-, NO_3^-, NO_2^-, SO_4^{2-}, CH_3COO^- is tolerated. However, neither of these two rare earths could be estimated in presence of each other. It is also found that Cu^{2+}, Fe^{3+}, MnO_4^-, Ti^{4+}, Pr^{3+} and Nd^{3+}, even in small amount, interfere seriously.

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Polarographic Determination of Stannous (tin) with Acrylic Acid

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Stannous (tin) produces a well defined diffusion controlled, irreversible reduction wave in acrylic acid which has been employed for its determination. The limiting current increased with the increase in the Sn(II) concentration. The possibility of determining mg quantities of Sn(II) in solution by this method has been examined. The variation in acrylic acid concentration has no effect on the shape of the polarogram. However, the value of half wave potential shifted to more negative potential with increase in acrylic acid conc. and the *p*H of solution. The value of half wave potential and diffusion current constant came out to be −0.476 S.C.E. and 3 02 vs, respectively in 0.1 *M* acrylic acid. A 10 fold ratio of In(III), Cu(II), Sn(IV), Pt(IV), Te(VI), Co(II), Ni(II), Zn(II), Mn(II), Al(III) and Fe(III) does not interfere. However, Pb(II) and Tl(I) interfere but their relatively lower amounts could be tolerated. The method is one of the most selective.

POLAROGRAPHIC reduction of stannous (tin) has been studied in a number of supporting electrolytes. The polarographic characteristics of stannous are very favourable for practical analytical purposes. The reduction wave in various supporting electrolytes, such as hydrochloric acid, nitric acid, perchloric acid, sulphuric acid, phosphoric acid, sodium fluoride, sodium tartrate-sodium hydroxide[1], ammonium acetate-acetic acid[2], sodium formate[3], hydrochloric acid-ammonium chloride-ascorbic acid[4], potassium hydrogen phosphate-citric acid[5] and lactic acid[6] has been reported. In most of the supporting electrolytes, a maximum appears and it gives a double wave, one anodic and other cathodic. In the present paper, a polarographic method has been developed for the determination of stannous (tin) using acrylic acid as a ground electrolyte. The method does not require external adjustment of *p*H, maximum suppressor and addition of any other auxiliary electrolyte. Interference of various ion has been studied in detail. Stannic (tin) does not undergo reduction at all in this medium. The method may be used for the determination of stannous (tin) in pure solution as well as in complex mixture.

Experimental

All polarograms were recorded at 25±0.1° with a manual Toshniwal polarograph. *p*H measurements were made with a Philips *p*H meter. The dissolved oxygen was removed by passing nitrogen through the cell solution for about 5 min before recording the polarograms. A saturated calomel electrode and a dropping mercury electrode with a capillary constant, $m^{2/3}t^{1/6}$ was 1.96 in distilled water and on open circuit were used. Stannous chloride solution and adjustment of *p*H were made with hydrochloric acid. The resistance of the cell was less than 200 ohms, so no correction for the IR drop through the cell was necessary. The reproducibility of the half wave potential was ± 1 mV. The experimental conditions were selected to maintain constant liquid junction potentials as much as possible.

The effect of *p*H was studied in *p*H range of 1 to 2. The $E_{1/2}$ shifted to more negative potential with the increase in *p*H. The reduction wave remained well defined in this *p*H range. So all the polarograms were recorded at *p*H 2 as there was no need of *p*H adjustment.

A variation of acrylic acid concentration from 0.1 *M* to 0.5 *M* had no effect on the shape of the polarogram. The diffusion current decreased while the value of $E_{1/2}$ shifted to more negative potential with the increase in acrylic acid concentration indicating the increase in the stability of stannous acrylic acid complex.

Polarograms were recorded for different concentration of stannous (0.2 m*M* to 1.2 m*M*) in 0.1 *M* acrylic acid. A linear plot passing through the origin was obtained when diffusion current (after correcting for the residual current) was plotted against stannous concentration, suggesting that this reduction can be used for the quantitative determination of stannous (tin).

Results and Discussion

The effect of the height of the mercury column on the diffusion current was also studied. The linear plot of i_d vs $\sqrt{h}$ showed the diffusion controlled nature of the reduction, which was already suggested by the linear plot of diffusion current vs stannous concentration. When $E_{d.e.}$ was plotted against log $\frac{i}{i_d - i}$ a straight line was obtained. The slope of this log plot and the value of $E_{3/4} - E_{1/4}$

were both −46 mV and were not in agreement with theoretical values, indicating the irreversible nature of the electrode reduction at d. m. e. Due to this irreversibility no deduction can be made about the nature of the complex formed. The value of I was calculated from Ilkovic equation and was found to be 3.02. This showed that stannous undergoes two electron change during the reduction process. Hence, the reduction can be shown as Sn(II) → Sn(O). Taking all the experimental observations into consideration, 0.1 *M* acrylic acid is found suitable for the estimation of stannous.

Interferences: Polarograms recorded in the presence of 10 fold amounts of W(VI), Sn(IV), Pt(IV), Te(IV), Mn(II), Ni(II), Zn(II), Co(II), Cr(III), U(VI), Fe(III), Pb(II), Sb(III) and Tl(I) revealed that only Pb(II) and Tl(I) interfered but their relatively lower amounts (Pb, 0.020 mg and Tl, 0.025 mg) could be tolerated. The results of the analysis of Sn(II) in presence of various ions are given in Table 1.

TABLE 1—EFFECT OF DIVERSE IONS (1 mg)

Diverse ion	Sn(II) Taken (mg)	Sn(II) Found (mg)	Error (%)
Fe(III)	0.88	0.88	0
Cu(II)	0.88	0 86	−2.2
Pt(IV)	0 88	0 86	−2.2
Mn(II)	0.88	0.88	—
Ni(II)	0.88	0 89	+1.1
Zn(II)	0 88	0 87	−1 1
Co(II)	0 88	0 88	—
Cr(III)	0.88	0 87	−1.1
U(VI)	0 88	0 90	+2.2
Se(IV)	0 88	0.88	—
Te(VI)	0 88	0 88	–
Sb(III)	0 88	0.90	+2 2
As(III)	0.88	0 88	—
Zr(IV)	0 88	0.88	—
Th(IV)	0.88	0.87	−1.1

Simultaneous determination of Sb(III)—Sn(II): As indicated in a preliminary observation, antimony do not interfere under these conditions. Based upon this fact, a method has been developed for the simultaneous determination of Sb(III) − Sn(II). A series of polarograms of solutions of mixed metal ions in 0.1 *M* acrylic acid were recorded. The value of diffusion current measured for each metal ion was referred to their respective calibration graph as before. The results observed for some mixture are given in Table 2.

TABLE 2—SIMULTANEOUS DETERMINATION OF Sb(III) - Sn(II)

Amount taken (mg)		Amount found (mg)		%Erro	
Sb(III)	Sn(II)	Sb(III)	Sn(II)	Sb(III)	Sn(II)
1.2715	2.07	1 2710	2 07	−0.04	0
1.5719	2.97	1 5719	2 90	0	−2.35
1.2715	2.07	1.2700	2.07	−0 11	0
2.1269	2 97	2.1250	2.90	−0 09	−2 35

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Complex Formation of Vanadium(V) with Salicylhydroxamic Acid in MIBK : Photometric Methods of Determination of Vanadium in Alloy Steel and Ores

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Reactions of vanadium(V) with N-salicylhydroxamic acid under varying conditions of pH and acidity and extraction behaviour of binary and ternary complexes in methyl isobutylketone are reported. New sensitive and selective photometric methods for trace determination of vanadium(V) in absence or presence of thiocyanate and its applications in the analyses of high speed steel, ilmenite and bauxite are also described.

IN this paper we report the use of a hydroxamic acid (N-SHA) where a phenolic $-OH$ group is attached to the *ortho* position of the phenyl ring[1-3]. In N-AHA molecule a basic $-NH_2$ group is attached to *ortho* position and the mixed-ligand extraction has been described[4]. Formations of different complexes of vanadium(V) with N-SHA under varying conditions of *p*H have been investigated along with ternary extraction involving thiocyanate. The sensitivity and selectivity of the determinations have been found to increase considerably both in binary and ternary extractions in methyl isobutylketone (mibk) even in presence of moderate excess of Fe(III) and Ti(IV). Fe(III) and Ti(IV) interferred in almost all the procedures mentioned with N-arylhydroxamic acids and amines either in extraction or in direct measurement in aqueous medium. Analyses of standard alloy steel, ilmenite and bauxite were also undertaken and the methods worked successfully[5-7].

Experimental

Reagents and solutions : A stock solution of vanadium was prepared from ammonium vanadate (E. Merck) and standardized[8]. The reagent, N-SHA, was prepared by the reported method[9]. Standard reagent solutions (1% w/v) and of desired strengths in pure mibk were used directly for extractions. A standard 2% aqueous solution of ammonium thiocyanate was used in ternary extraction. All other chemicals, reagents and solvents used in the experiments were of A. R. grade quality.

Apparatus : Measurements were made with Hilger-Uvispek and Spektromom 204 spectrophotometers with matched 1 cm quartz or glass cells. A Systronics *p*H-meter (324, India) was used for *p*H measurements.

Recommended procedure :

(A) *Binary extraction*, p*H 3.1 :* An aliquot of vanadium solution (1.963×10^{-3} *M*) was taken in a 100 ml separatory funnel and the *p*H was adjusted by adding very dil HCl after 5 ml of 1% reagent was added to 10 ml of aqueous phase and 0.5 ml of 0.1 *M* HCl. It was shaken with an equal volume of organic phase (10 ml) for 5 min. The blue-violet complex extracted from *p*H 3.1 was drained out in a 50 ml beaker and dried with anhydrous sodium sulphate. The extractions were repeated with 5 ml portions of the solvent. The combined extract was transferred into a 25 ml volumetric flask. The volume was made up to the mark with pure solvent. The absorbance of the complex solution was measured at 575 nm against solvent blank. A calibration curve was constructed.

(B) *Binary extraction, 1.8* M *HCl :* An aliquot of the metal solution (1.963×10^{-3} *M*) was taken in a 100 ml separatory funnel with 5 ml of 1% reagent. The *p*H was adjusted to 3.1 by adding 0.5 ml of 0.1 *M* HCl and the mixture was shaken with 10 ml of methyl isobutyl ketone. The acidity was then adjusted to 1.8 *M* HCl by adding 6 *M* HCl. The wine-red complex was extracted for 5 min. It was dried and transferred into a 25 ml volumetric flask and made up to the mark. The absorbance was measured against solvent blank at 510 nm. A calibration curve was also constructed.

(C) *Ternary extraction*, p*H 0.95/0.16* M *HCl :* In the ternary extraction, the blue-violet complex was first extracted at *p*H 3.1 by adding 5 ml of 1% reagent and 0.5 ml of 0.1 *M* HCl for 2 min with 15 ml of methyl isobutyl ketone. 1 ml of 2% ammonium thiocyanate was added and the *p*H of the 15 ml aqueous phase was adjusted to 0.95. The blue-violet complex was again extracted for 8 min. The extractions were repeated with 5 ml portions of the solvent. The organic layer was dried over anhydrous sodium sulphate, transferred into a 25 ml volumetric flask and made up to the mark with pure solvent. A reagent blank was prepared similarly. The absorbance of the complex was measured against solvent

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at 540 nm. A calibration curve was also constructed.

Procedure for steel analysis: 0.5 g of steel sample was dissolved in 25 ml dilute sulphuric acid (1 : 1) and the solution was digested on a hot plate to a syrupy solution, repeating the addition of acid. It was then treated with 5 ml of conc nitric acid for complete digestion and evaporated to dryness. The solution was diluted with 50 ml water, boiled, filtered, and washed with hot acidulated water and finally with hot water. The cold filtrate and the washings were taken in a 250 ml volumetric flask and the volume was made up to the mark. An aliquot of the steel solution was transferred and oxidised at room temperature with 0.1% $KMnO_4$ solution till the pink colour persisted. A hot solution of 15% NaOH solution was then added and the mixture boiled. The precipitate was filtered off and redissolved in dil HCl and the procedure was repeated several times. The filtrates were collected and boiled down to a low volume. The solution was cooled and vanadium content was determined following the recommended procedures A, B and C. The absorbance of the extracts was measured at 575, 510 and 540 nm for the respective complexes and the metal content determined separately.

Procedure for ore analysis 0.5 g of finely powdered ore was fused with 9 g $KHSO_4$ and a few drops of H_2SO_4 in a silica crucible over a low flame to avoid spurting and a clear melt was obtained. The fused mass was cooled and leached with 1 . 9 H_2SO_4 acid. The solution was boiled and oxidised with a few drops of nitric acid. Iron and titanium was precipitated as hydroxides with an excess of 15% NaOH solution. Any adsorbed vanadium in the hydroxide was freed by double precipitation method. The filtrates were combined and the volume reduced to 0.5 ml by boiling. The cold solution was transferred into a 100 ml standard flask and the volume was made up with water. Different aliquots were taken and the metal was determined by procedures A, B and C using fluoride for traces of iron and titanium in the solution.

Procedure for bauxite · Bauxite sample was decomposed by alkaline flux. 0.5 g of the sample was fused for 2 hr with Na_2CO_3 (3-4 g) and NaOH (1 g) in a nickel crucible. The melt was cooled and leached with hot water and kept overnight. The aqueous extract of vanadium and other insoluble materials along with iron and titanium was filtered, transferred into a 100 ml volumetric flask and the volume made up to the mark. The vanadium content was determined using appropriate amount of the solution.

Results and Discussion

Absorbance spectra: The absorbance spectra of binary and ternary chelates of vanadium(V) showed maximum at 575, 510 and 540 nm (Fig. 1). Since reagent blanks showed no absorbance in these regions the absorbance has been measured against solvent blank mibk.
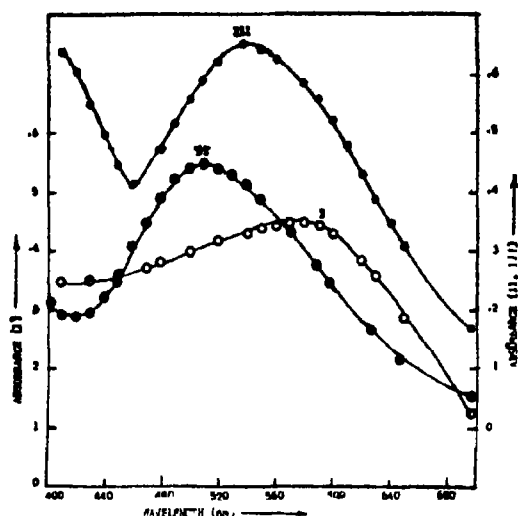
Fig 1 Spectral curves of the V(V) binary and ternary complexes V(V) = 7.858 × 10^{-4} *M*, N-SHA = 1.806 × 10^{-3} *M*, NH_4SCN = 5.255 × 10^{-2} *M*.
Curve I – ○ : V(V)-N-SHA binary complex at *p*H = 3.1,
II – ○ : V(V)-N-SHA binary complex at 1.8 *M* HCl,
III – ● : V(V)-N-SHA ternary complex at *p*H = 0.95

Optimum reaction conditions: The optimum *p*H range of extractions for blue-violet chelate was found to be 2.2-5.6 and *p*H was always adjusted to 3.1 for all measurements. At *p*H < 2.2 a shift of the maximum occurs with corresponding colour change towards red-violet. The intensity of wine-red complex is constant in the region 0.6-4.2 *M* HCl. It was observed that direct addition of 6 *M* acid produced a very low absorbance. The complex is first extracted from *p*H 3.1 and then the acidity increased. An emulsion, requiring time to break, formed as acidity increased above 3.5 *M* HCl. All measurements were made at 1.8 *M* HCl for wine-red complex. The optimum acidity range for violet coloured mixed-ligand vanadium complex is *p*H 1.3 to 0.33 *M* HCl. This complex is formed from *p*H 1.8 to 3.0 *M* HCl, and separation and extraction is slow at *p*H > 1.8 and > 0.8 *M* HCl due to emulsion formation. Ternary extractions were made at *p*H 0.95/0.16 *M* HCl. The binary complex is first extracted from *p*H 3.0 and then a 0.16 *M* HCl acidity was maintained.

2.5 ml of 1%, 2.0 ml of 1% and 0.5 ml of 1% (w/v) reagent in mibk were found sufficient for full colour development of the respective complexes and their extractions. The optimum range is 2 to 10 ml of 1% for binary systems and 0.5-10 ml of 1% reagent for ternary system. 5 ml of 1% reagent was used for all three extractive methods. Ternary complex is formed with 0.1 to 12 ml of 1% reagent with a fixed amount [1 ml of 2% (0.26 *M*)] of thiocyanate added and 0.5 ml of 1% reagent. With 5 ml of 1% reagent (N-SHA) the violet complex of vanadium(V) was formed with 0.01 to 10 ml of 2%

ammonium thiocyanate and 0.75 ml was found sufficient. A 5 ml of 2% solution was always used in the method.

The binary and ternary complexes are completely extracted within 4 to 5 and 7 to 9 min and show constant absorbance immediately after the volume is made up. The complexes are stable for more than 24 hr at room temperature (27°).

Calibration curve, optimum range and sensitivity : For solutions of varied amount of vanadium(V), fixed amounts of reagent (N-SHA) and thiocyanate solutions were utilized in the above procedures and absorbances were measured at 575, 510 and 540 nm, respectively. The systems obeyed Beer's law (Fig. 2) in the range 0.2-8 (blue-violet), 0.25-9 (wine-red) and 0.4-12 (violet) ppm
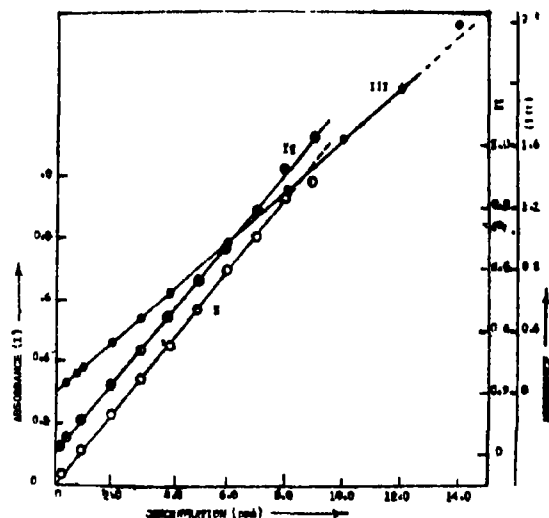
Fig 2. Beer's law curves N-SHA = 1.306×10^{-2} *M*, NH_4SCN = 5.255×10^{-2} *M*.
Plot I – ○. V(V)-N-SHA binary complex at *p*H = 3.1.
II – ○ : V(V)-N-SHA binary complex at 1.8 *M* HCl,
III – ● : V(V)-N-SHA-SCN ternary complex at 0.16 *M* HCl

with optimum range obtained from Ringbom's plot[9] as 2-6.5, 2-6 and 1-6 ppm, respectively. The % relative error per 1% absolute photometric error using Ayres' equation[10] for the systems are 2.71, 2.72 and 2.73%, respectively.

The molar absorptivities are 5.71×10^3 (at 575 nm), 5.73×10^3 (at 510 nm) and 8.34×10^3 (at 540 nm) l. mole^{-1} cm^{-1}. The corresponding Sandell sensitivities[11] are 0.00893, 0.0089 and 0.0061 μg cm^{-2} V(V).

Interference studies : Solutions were prepared by the above procedures with 4 ppm vanadium(V) (25 ml) and different amounts of diverse ions at the *p*H acidity conditions. The ions were added before the reagent. Normally, Fe(III), Ti(IV), Mo(VI), W(VI), Zr(IV), Nb(V), Hf(IV) have low tolerance limits. Masking with fluoride ion is effective for moderate excess. Most of the metal ions do not interfere in all the three systems. Anions have no other effect. The methods were found to be accurate and precise for analyses of geological materials and alloy. The results are summarized in Table 1.

Table 1—Effect of Diverse Ions
[V(V) = 0.1 mg, N-SHA = 1% in mibk, NH_4SCN = 2% aq. solution]

Ions	Tolerance limits, mg		
	*p*H 3.1 575 nm	1.8 *M* HCl 510 nm	*p*H 0.95 540 nm
Acetate	10	10	20
Fluoride	20	10	20
Tartrate	50	45	30
Oxalate	2	8	20
Citrate	50	50	25
EDTA	1.5	40	10
Phosphate	10	75	50
Fe(III)	1	1.25	5*
Ti(IV)	Int.	1	5*
Mo(VI)	1.5	1.25	1.25*
W(VI)	1	4.5	2.5*
Zr(IV)	5	6.25	6.25*
Hf(IV)	5	6.25	6.25*
Th(IV)	10	20	10
Nb(V)	1.25	1.25	1.25*
Ta(V)	1.25	1.25	3*
UO_2(II)	7.5	11.25	10
Co(II)	15	20	5
Ni(II)	10	15	5
Cu(II)	2.5	7.5	3.75
Mn(II)	4	20	12.5
Cr(III)	7.5	15	10
Al(III)	2.5	5	5
Zn(II)	7 5	15	10
Cd(II)	6.25	6.25	12.5
Pb(II)	10	20	15
Pd(II)	0.75	3.75	1

*Fluoride masking.

Determination of vanadium in steel, rock and ore : The ilmenite samples were collected from Hornbendite rock of Tamil Nadu and Putkapahar of M.P. (GSI samples) and bauxite from Indian Oxygen Limited. These were finely powdered (200 mesh) and obtained directly after separation and the samples were standardized previously by spectroscopic methods. The present methods are found useful and the results of the analyses by the procedures are found to agree well with each other. The amounts of vanadium present in the samples from analyses report are given in the following Table 2. The present solvent extraction method is simple and rapid over the other existing methods.

Table 2—Analyses of Alloy Steel (BAS 64b), Rock (Ilmenite) and Ore (Bauxite)

Methods	BAS steel 64b, certified 1.99% V	Rock (ilmenite mineral), certified 0.1% and 0.15% V		Ore (bauxite), certified > 0.08%
Binary (3.1 *p*H)	1.97*	0.09	0.14	0.26
Binary (1.8 *M* HCl)	1.965	0.08	0.138	0.26
Ternary (0.16 *M* HCl)	1.97	0.09	0.14	0.26

*Values are average of several determinations.

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NOTES

Azo Complexes : Complexes of Alkali Metal Salts of Some Organic Acids with *o*-Hydroxybenzene-Azo-2-Naphthyl Amine

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As an extension of our previous work[1,2] on azo complexes, we are reporting the synthesis of alkali metal salt adducts of *o*-hydroxybenzene-azo-2-naphthylamine (OHBANM), which have two electron releasing groups $-OH$ and $-NH_2$ in the *o* and *o'* positions to the azo group ($-N=N-$) and hence would increase the donor property of the azo group. Intramolecular hydrogen bonding in the ligand plays an important role in adduct formatiom.

Experimental

The ligand OHBANM was prepared by standard method[3] (m. p. 192-193°). Solutions of the alkali metal salts used were prepared in 95% ethanol.

The general method of preparation was to add the alkali metal salts of organic acids to hot absolute ethanolic solution of OHBANM in mono molecular ratio. The mixture was refluxed over hot plate using magnetic stirrer for about 1 hr. The solution, on keeping, yielded crystalline solid adducts. The crystals were filtered, washed with absolute ethanol and dried in an oven at 90°.

Results and Discussion

The adducts are stable when stored under dry condition e.g. in a desiccator, but decompose in the presence of moisture. The adducts are thermally stable. When heated, they undergo decomposition at a temperature higher than the melting point of the ligand suggesting them to be pure compounds. The compounds are sparingly soluble in hot polar solvent. The colour, melting or decomposition temperatures and analytical data of the compounds are given in Table 1.

The presence of electron releasing $-OH$ and $-NH_2$ groups at *o* and *o'* positions to the azo group increases the coordinating capacity of the azo-nitrogen which perhaps takes part in association. The NH_2, $O-H$ and $-N=N-$ frequencies of ligand and adducts are listed in Table 2.

In ligand OHBANM, we observe that the two $N-H$ stretch vibrations appear as medium peaks at $\sim 3325\ cm^{-1}$ and $\sim 3260\ cm^{-1}$. In the alkali metal adducts, the $\sim 3325\ cm^{-1}$ band remains unaffected after association, but the $\sim 3260\ cm^{-1}$ band shifts down to $\sim 3125\ cm^{-1}$. It suggests that there has been decrease in the bond order of $N-H$. The OH group in the ligand is hydrogen bonded and does not show up at the original place. In OHBANM adducts with alkali metal salts, the $O-H$

TABLE 1

Compound	Colour	Melting/decomp. (d) temp (°C)	Found (%)				Calcd. (%)			
			C	H	N	M	C	H	N	M
OHBANM = L	Deep violet	193	72 98	4 89	16 01	—	73 00	4.94	15.99	–
Na1N2N L	Brown	209(d)	68 10	4 45	12 57	4 92	68 11	4 13	12 23	5.02
K1N2N.L	Brown	213	65 65	4 22	11 99	8 11	65 82	4 01	11.81	8 22
Li8HQ.L	Deep green	237	72 25	4 79	13 84	–	72 46	4 58	13 52	1.69
Na8HQ.L	Deep green	232	69.15	4 62	13 84	5 11	69 74	4.41	13.02	5.34
K8HQ L	Brown	245	67 11	4 47	12 87	8 34	67 26	4.26	12.55	8 74
NaONP.L	Deep green	225	62.11	4 24	13 51	5.12	62.26	4.01	13.20	5 42
KONP.L	Red	228	59 89	4 01	12.93	8 85	60 00	3 86	12 72	8 86
Na2H3NA L	Red	242	68 12	4 41	9 11	4 21	68 49	4 22	8.87	4.86
K2H3NA L	Deep green	246	66 14	4 21	8 96	7 42	66.25	4 08	8.58	7 97
Na anth L	Bright red	225	65 12	4 71	13 57	5 12	65 40	4 50	13 27	5 54
K anth.L	Deep green	215	63 44	4.36	12.87	8 46	63 01	4 33	12.78	8.70
NaSalA.L	Brown	233	65.43	4 44	10.21	5 12	65.24	4.25	9 92	5.43
KSalA.L	Deep red	227	62.42	4 32	10.11	8 23	62.87	4 10	9 56	8.88
NaSalH.L	Reddish brown	226	67.51	4 73	10 72	5 12	67 81	4 42	10 31	5.65
Na.acac.L (Soluble in ethanol)	Royal blue	–								

1N2N = 1-nitroso-2-naphthol, 8HQ = 8-hydroxyquinoline, ONP = *o*-nitrophenol, 2H3NA = 2-hydroxy-3-naphthoic acid, anth = anthranilic acid, SalA = Salicylic acid, SalH = Salicylaldehyde, acac = acetylacetone.

TABLE 2

Compound	N–H frequencies (cm^{-1})	O–H frequencies (cm^{-1})	–N=N– frequencies (cm^{-1})
OHBANM=L	3325 3260		1535
Na1N2N.L	3325 3125	2450 1960	1525
K1N2N.L	3325 3150-25	2450 1920	1505
NaONP.L	3325 3125	2400 1940	1510
KONP.L	3325 3115	2400 1860	1507
Na2H3NA.L	3300 3225	2400 1880	1530
K2H3NA.L	3325 3125	2400 1880	1530
Na8HQ.L	3350(br)		1505
NaSalH.L		2380 1860	1500
KSalA.L		2380 1860	1505

br = broad.

frequencies show up as one or two broad humps, one at ~ 2500 cm^{-1} and the other at 1800-1960 cm^{-1}. It suggests strong association of the OH group.

The –N=N– stretching frequency at 1535 cm^{-1} in the ligand has been spotted between 1525 cm^{-1} to 1500 cm^{-1} in the adducts, suggesting again the association of –N=N– group in the alkali metal adducts.

Our present work also shows that strong intramolecular hydrogen bonding existing in the ligand breaks on complexation. It has been further observed that ligands, which have stronger intrahydrogen bonding, form stable alkali metal adducts.

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Interaction Products of Triphenylphosphine Oxide with Some Organotin Halides

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COMPLEXES of triorganophosphine oxide with a variety of metal salts have been extensively studied[1-5]. Syntheses and characterisation of adducts of the Lewis base with organometallic moieties have also been reported[6-16]. Molecular addition compounds of triphenylphosphine oxide (TPPO) with organotin moieties appear not to have received adequate attention. In continuation of our studies on organotins[17-21], we report here the *interaction of TPPO with some organotins which* yielded molecular addition compounds of the type $R_nSnX_{4-n}.L$ (R = phenyl or butyl; X = Cl or Br, n = 1,2 or 3 and L = TPPO). The compounds have been characterised by elemental analysis, melting point and their data on conductance, molecular weight, ir and mass spectrometry have been discussed.

Experimental

Di or triorganotin halides were prepared according to literature methods[22]. TPPO (Carlsile) and other reagents of analytical grade (B.D.H./S. Merck) were used without further purification.

In a typical reaction, 2 m mole of an organotin derivative and equimolar amount of TPPO were refluxed in 40 ml of benzene/chloroform for about 1 hr. A suitable volume of pet. ether (60-80)/ether was added to this (in some cases reaction mixture was kept in a fridge) and the solid so obtained was separated, washed with pet. ether, recrystallised from benzene-pet. ether solvent pair and dried under vacuum. The yield was about 66%.

The m. ps. of the adducts were determined on electrically operated apparatus (M/s. Toshniwal Bros., Bombay). Elemental analyses were done by micro analytical method but tin was estimated as stannic acid. The metal was weighed as oxide after ignition.

The infrared spectra of TPPO and their adducts with organotins were recorded in the region 4000-200 using Perkin Elmer IR spectrophotometer, model 521. Calibration was performed with a polystyrene film.

Conductance was measured in benzene by Philips, type PR 9500, conductivity bridge using dip type conductivity cell having a cell constant 0.7584. The molecular weights of the adducts were determined cryoscopically in benzene. Mass spectrometer, Hitachi model No. RMU-6E, was used for obtaining mass spectra.

Results and Discussion

Experimental data of the adducts are given in Table 1. The adducts melt in the range of 62-175° while Ph-SnCl_3.TPPO do not melt up to 250°. They are soluble in common organic solvents, are thermally stable and do not decompose when heated to their m. ps. for several hr. They are insensitive to atmospheric moisture but easily hydrolyse when refluxed with water or aqueous ammonia yielding polymeric organotin oxide as the final product The conductance values in $10^{-3}M$ solutions indicate

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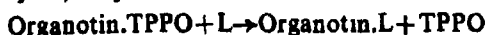
Table 1—Experimental Data for Triphenylphosphine Oxide (L) of Organotin Halides

Adducts	m.p (°C)	Sn	C	N	Mol wt.	IR absorption (cm^{-1}) νP=O	νSn−O
$PhSnCl_3.L$	>250	20.2 (20.4)	50.0 (49.6)	3.2 (3.4)	450 (581)	1145 m	320 s
$Ph_2SnCl_2.L$	175	19.4 (19.1)	57.6 (57.8)	4.2 (4.0)	422 (622)	1140 s	318 s
$Ph_2SnBr_2.L$	158	15.4 (16 7)	50.6 (50.6)	3.1 (3.5)	602 (711)	1135 s	315 s
$Ph_3SnCl.L$	170	17.1 (17.9)	66.8 (66.5)	4.7 (4.5)	510 (664)	1155 s	320 s
$BuSnCl_3.L$	88	20.9 (21.2)	47 3 (47.1)	4.2 (4.3)	400 (560)	1150 s	325 s
$Bu_2SnCl_2.L$	62	20.3 (20.4)	53.5 (53.6)	5.6 (5.7)	487 (582)	1153 s	335 s
$Bu_2SnBr_2.L$	78	18.4 (17 7)	46.3 (46.5)	5.1 (4.9)	498 (671)	1148 m	322 m

Figures in parenthesis are the calculated values, m = medium, s = strong.

the absence of ionic species and their observed low molecular weight, compared to formulae weight, suggest significant dissociation in solution.

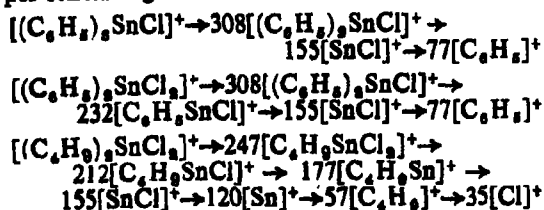
As per equation below, the interaction of the adducts with some Lewis bases such as 1,10-phenanthrolene, 2,2′-bipyridine, dimethylsulfoxide, pyridine-N-oxide was investigated in chloroform pet. ether. The complete substitution of TPPO molecule by the above bases indicates its comparatively poor donor ability towards the investigated Lewis acids. These replacements were confirmed by elemental analyses, m. ps. and infrared data of the adducts.

$$\text{Organotin.TPPO} + \text{L} \rightarrow \text{Organotin.L} + \text{TPPO}$$

(L = 1,10-phen, 2,2′-bipy, py-N-oxide or DMSO)

Mass spectra* of three adducts having different Lewis acid species $(C_6H_5)_3SnCl$, $(C_6H_5)_2SnCl_2$ and $(C_4H_9)_2SnCl_2$ were recorded as an aid to their characterisation and to study their fragmentation pattern. On electron impact, the adducts readily break up into their Lewis acid and Lewis base fragments viz. $[(C_6H_5)_3SnCl]^+$ (m/e 386) or $[(C_6H_5)_2SnCl_2]^+$ (m/e 344) or $[(C_4H_9)_2SnCl_2]^+$ (m/e 304) and $[(C_6H_5)_3PO]^+$ (m/e 278) while the molecular ions were not observed. This indicated a weak linkage between the acids and the base forming the adducts. The fragment $[(C_6H_5)_3PO]^+$ gave rise to smaller fragments m/e 201 $[(C_6H_5)_2PO]^+$, 108 $[C_6H_5P]^+$, 47$[PO]^+$, 31$[P]^+$ on further cleavage. The fragmentation pattern of $[(C_6H_5)_3SnCl]^+$, $[(C_6H_5)_2SnCl_2]^+$ and $[(C_4H_9)_2SnCl_2]^+$ was dissimilar and gave mass spectral peaks (m/e) as per schemes given below :

$$[(C_6H_5)_3SnCl]^+ \rightarrow 308[(C_6H_5)_2SnCl]^+ \rightarrow 155[SnCl]^+ \rightarrow 77[C_6H_5]^+$$

$$[(C_6H_5)_2SnCl_2]^+ \rightarrow 308[(C_6H_5)_2SnCl]^+ \rightarrow 232[C_6H_5SnCl]^+ \rightarrow 155[SnCl]^+ \rightarrow 77[C_6H_5]^+$$

$$[(C_4H_9)_2SnCl_2]^+ \rightarrow 247[C_4H_9SnCl_2]^+ \rightarrow 212[C_4H_9SnCl]^+ \rightarrow 177[C_4H_9Sn]^+ \rightarrow 155[SnCl]^+ \rightarrow 120[Sn]^+ \rightarrow 57[C_4H_9]^+ \rightarrow 35[Cl]^+$$

* The mass spectral fragments under consideration refer to appropriate combination of abundant isotopes for Sn and Cl.

The most significant absorption in the infrared spectra of TPPO and its adducts, the P=O stretching frequency appearing as a strong band at 1190 cm^{-1} in the spectrum of the Lewis base, undergoes a negative shift of 37 cm^{-1} to 55 cm^{-1} on adduct formation. This lowering of P=O is indicative of coordination[7-9,13,14].

A new spectral band of strong intensity has been observed in a close range of 315-335 cm^{-1} in the spectra of adducts which was not present either in the spectra of TPPO or the Lewis acids. This band may possibly be associated with vibration of O→Sn. Sn−Cl and Sn−aryl stretches have been found at the known positions in the spectra of the Lewis acids[17,18]. A significant lowering of Sn−Cl stretching in the adducts characteristically depicts increase in the coordination number of the metal atom.

Investigations revealed some important biological properties of the adducts and the findings will be reported elsewhere.

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Mixed Ligand Cobalt(III) Complexes Containing Benzotriazole or 5-Nitrobenzotriazole

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COMPLEXING behaviour of benzotriazole[1-4] and its use in estimation of some transition metal ions[5-7] are well known. Preparation of mixed ligand Co(III) complexes of benzotriazole and of 5-nitrobenzotriazole from *trans*-[Co(en)$_2$Cl$_2$]Cl and [Co(NH$_3$)$_3$(NO$_2$)$_2$Cl] and their characterization by electronic and ir spectral study and magnetic measurements are reported in this paper.

Experimental

Trans-[Co(en)$_2$Cl$_2$]Cl[8], [Co(NH$_3$)$_3$(NO$_2$)Cl][9] and benzotriazole[6] were prepared by reported methods and 5-nitrobenzotriazole was prepared by a modification of the method for benzotriazole.

[Co(en)$_2$(Bt)*Cl]Cl (rose red) and [Co(en)$_2$(NO$_2$-Bt)Cl]Cl (orange red) were obtained by treating an aqueous solution of [Co(en)$_2$Cl$_2$]Cl with an aqueous ethanolic solution of benzotriazole and 5-nitrobenzotriazole respectively in 1 : 1 molar ratio and adjusting the *p*H to 7 with dil. NaOH. [Co(NH$_3$)$_3$-(NO$_2$)$_2$(Bt)].H$_2$O (orange yellow) and [Co(NH$_3$)$_3$-(NO$_2$)$_2$(NO$_2$-Bt)].1.5H$_2$O (dull orange yellow) were prepared in a similar way from [Co(NH$_3$)$_3$-(NO$_2$)$_2$Cl]. [Co(en)$_2$(Bt)Cl] I.2H$_2$O (orange red) was precipitated by adding a saturated aqueous solution of KI to an aqueous solution of [Co(en)$_2$-(Bt)Cl]Cl.

Cobalt in the complexes was estimated as cobalt sulphate after igniting the complex and treating the residue with conc. HNO$_3$ and conc. H$_2$SO$_4$. Nitrogen was estimated by Duma's semi-micro method. Water of crystallization was determined by heating the complex below 120° and chlorine was estimated as AgCl by decomposing the complex in presence of AgNO$_3$. C and H analyses were obtained from microanalytical laboratory.

Magnetic susceptibilities were measured by Guoy method using Hg[Co(CNS)$_4$] as standard. Effective magnetic moments were calculated after making diamagnetic correction using Pascal's constants[11]. Conductivity measurements of aqueous solutions were done on a conductivity bridge (Toshniwal, India). Electronic spectra were recorded on a Hilger Watts Uvispek spectrophotometer H700. Infrared spectra (4000-650 cm^{-1}) were recorded in KBr discs on a Perkin Elmer spectrophotometer.

Results and Discussion

Substitution products from trans-[*Co*(*en*)$_2$*Cl*$_2$]*Cl* : The analytical data of the complexes are reported in Table 1. The complexes are slightly soluble in water but almost insoluble in methanol or ethanol. They are diamagnetic suggesting the presence of octahedral low spin Co(III)[12]. Λ_M values of freshly prepared 10^{-3} *M* aqueous solutions of [Co(en)$_2$(Bt)Cl]Cl and [Co(en)$_2$(NO$_2$-Bt)Cl]Cl were 125 and 130 ohm^{-1} cm^2 mol^{-1}, respectively which are in the range of 1 : 1 electrolytes[13]. The conductance gradually increased on standing which may be due to aquation e.g. [Co(en)$_2$(Bt)Cl]$^+$ + H$_2$O = [Co(en)$_2$(Bt)(H$_2$O)]$^{2+}$ + Cl$^-$.

These complexes show only one weak band around 500 nm (Table 1) except [Co(en)$_2$(Bt)Cl]Cl which displays an additional shoulder at 370 nm. The weak band corresponds to $^1A_{1g} \rightarrow {}^1T_{1g}$ and the shoulder to $^1A_{1g} \rightarrow {}^1T_{2g}$ transition of low spin octahedral Co(III) complexes[14]. Higher λ_{max} values for the solid state than for the solution (Table 1) indicate lower symmetry in solid than in solution. *Cis*- and *trans*-isomers of the complexes of the type [CoA$_4$BC]$^{n+}$ can be differentiated by ϵ_{max} values of these bands[14b], e.g. ϵ_{max} values of $^1A_{1g} \rightarrow {}^1T_{1g}$ bands of *cis*-[Co(en)$_2$Cl$_2$]$^+$ and *cis*-[Co(en)$_2$(H$_2$O)(Cl)]$^{2+}$ are 89 and 90 compared to 41 and 40 for the corresponding *trans*-complex[15,16].

† Author for correspondence. * BtH = benzotriazole.

TABLE 1—ANALYTICAL RESULTS AND ELECTRONIC SPECTRAL DATA

Complex	Analysis%		$^1A_{1g} \rightarrow {}^1T_{1g}$ band	
	Calcd	Found	λ_{max} (nm)	ϵ_{max}
$[Co(en)_2(Bt)Cl]Cl$	Co 16.01	16.11	535[d]	–
	N 26.74	26.84	500[a]	117
	Cl 19.26	19.31		
$[Co(en)_2(Bt)Cl]I.2H_2O$	Co 11.90	12.01	530[d]	–
	N 19.78	19.81		
	C 24.28	24.41		
	H 4.88	4.91		
	H_2O 7.27	7.02		
$[Co(en)_2(NO_2-Bt)Cl]Cl$	Co 14.27	14.31	540[d]	–
	N 27.12	27.18	500[a]	128
	Cl 17.17	17.05		
$[Co(NH_3)_3(NO_2)_2Bt].H_2O$	Co 17.42	17.51	470[d]	–
	N 33.13	33.21		
	C 21.25	21.31		
	H 2.56	2.61		
	H_2O 4.23	4.01		
$[Co(NH_3)_3(NO_2)_2(NO_2-Bt)].1.5H_2O$	Co 14.96	15.02	475[d]	–
	N 32.07	32.18		

d=diffused reflectance, a=aqueous solution

In the present case, only one isomer has been obtained for each complex and hence such a comparison cannot be made. However, high ϵ_{max} values *viz.*, 117 for $[Co(en)_2(Bt)Cl]Cl$ and 128 for $[Co(en)_2(NO_2\text{-}Bt)Cl]Cl$ and similarity in the band structure in these complexes with the *cis*-complexes reported earlier[15,16] indicate *cis*-configuration in these complexes.

The reported diagnostic splittings of NH_3 deformation, NH_3 rocking[17,18] and also some NH vibration bands[19] cannot be applied in the present case for establishing *cis*- or *trans*-configuration since bands of benzotriazoles interfere in these regions. However, the presence of a large number of bands in the present case and the presence of two $-CH_2-$ rocking modes, *viz.*, 880 and 898 cm^{-1} for $[Co(en)_2(Bt)Cl]Cl$ and 872 and 890 cm^{-1} for $[Co(en)_2(NO_2\text{-}Bt)Cl]Cl$ may be indicative of *cis*-configuration in these complexes[20,21].

Substitution from $[Co(NH_3)_3(NO_2)_2Cl]$. These complexes, *viz.*, $[Co(NH_3)_3(NO_2)_2Bt].H_2O$ and $[Co(NH_3)_3(NO_2)_2(NO_2\text{-}Bt)].1.5H_2O$ are insoluble in water, methanol, ethanol, benzene or chloroform. They lose water molecules on heating at 100 without change in colour. They are slightly paramagnetic, $\mu_{eff}=0.71$ B.M. for the former and 0.75 B M for the latter. Their residual magnetism may be due to the formation of a little Co(II) or it may be due to second order Zeeman effect[22].

The ν_{as} and ν_s of NO_2^- are observed at 1395 cm^{-1} and 1330 (and 1318) cm^{-1} for $[Co(NH_3)_3(NO_2)(Bt)].H_2O$ and at 1400 cm^{-1} and 1332 (and 1308) cm^{-1} for $[Co(NH_3)_3(NO_2)_2(NO_2\text{-}Bt)].1.5H_2O$. The shift in ν_{as} of NO_2^- from 1250 cm^{-1} in free ion to ~ 1400 cm^{-1} in the complexes suggest N-bonding of NO_2^-[23] which is further confirmed by the absence of the characteristic ν_{as} band of nitrito group at 1065 cm^{-1}[24]. The δ (O–N–O) for these complexes are observed at 811 and 822 cm^{-1}, respectively Further, the observed splitting of the ν_{as} band of NO_2^- may be indicative of *cis*-arrangement of the two NO_2^- groups in the complexes.

It has not been possible to establish deprotonation of benzotriazoles in these complexes from the ir data because of the presence of N–H vibrations arising from ethylenediamine or ammonia. However, the necessity of alkaline medium for the formation of these complexes, their diamagnetic behaviour and their elemental analyses do confirm deprotonation.

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Mixed Ligand Complexes of Co(II), Ni(II), Cu(II) and Zn Salts with *o*-Hydroxy Propiophenone and Quinoline

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CHEMISTRY of metal β-diketonates has invoked[1] lot of interest in recent years in such diverse areas as spectral studies, gas chromatography, nmr shift reagents, laser technology and as radical initiators in polymerization reactions. The formation of adducts of metal β-diketone chelates plays an important role in the synergistic enhancement of solvent extraction of metal ions. β-Keto esters and *o*-hydroxy carbonyl compounds closely resemble the β-diketones. It was thought worthwhile to study the reactions of metal salts with *o*-hydroxy propiophenone and quinoline. As a result, this communication reports chelates of *o*-hydroxy propiophenone and their adducts with quinoline.

Experimental

Complexes of the type MLXQ or M'LXQ: Absolute ethanolic solution of metal salts was treated with *o*-hydroxy propiophenone and quinoline in 1 : 1 : 1 proportion and the resulting solution refluxed for 30 min. To this solution, dilute ammonium hydroxide was added dropwise under constant stirring till the *p*H was 7. The resulting precipitates were filtered, washed with ethanol and ether and dried in vacuum.

Complexes of the type ML_2Q_2 or $M'L_2Q$: Aqueous solutions of metal acetates were treated with ethanolic solution of *o*-hydroxy propiophenone in 1 : 2 proportion and the mixture stirred for 30 min at 40°. Metal chelates were filtered, washed with ethanol and ether and dried in vacuum. Ethanolic suspension of different metal chelates was treated with quinoline in 1 : 2 ratio and the resulting solution refluxed for 30 min. On concentrating the solution in a rotary vacuum evaporator and keeping at 10° overnight crystalline base adducts separated. These were filtered, washed with ethanol and dried in vacuum.

Analyses and physical measurements were done as reported earlier[2]. The relevant analytical data are presented in Table 1 and the spectral data in Table 2.

Results and Discussion

In the infrared spectra of hydroxy propiophenone ν(C=O) is observed[3] at 1620 and ν(O–H) at 3350 cm^{-1}. In monochelate complexes, ν(C=O) shifts to lower frequency region and is observed around 1600 cm^{-1} whereas ν(O–H) disappears. Thus the ligand anion forms the chelate using both the oxygen atoms. This has been substantiated by the observation[4] of ν(M–O), ν(M–N) and ν(M–Cl) around 440-460, 320-335 and 230-250 cm^{-1} region, respectively. Thus, these are four coordinated compounds involving the mono chelate, the coordinated anion and coordinated quinoline. In the nitrato complexes, the position of ν_4 and ν_1 (1410 and 1280 cm^{-1}) of NO_3 and their difference of the order of 130 cm^{-1} suggest[5,6] monodentate nitrate coordination.

In the *bis* chelates ν(C=O) is found around 1590-1600 cm^{-1} which shifts to slightly higher frequency region in the base adducts. The formation of the base adducts of the *bis* chelates has been confirmed[4] by the appearance of ν(M–O) and ν(M–N) around 460 and 320 cm^{-1} region in the far infrared spectra.

In the visible region, cobalt mono chelate complexes give rise to one intense absorption band around 16.0 kK region assignable[7] to $^4A_2 \rightarrow {}^4T_1(P)$ transition. Position of the band, its high intensity and lower magnetic moment value suggest a possible tetrahedral configuration for these complexes. The base adduct of the *bis* chelate complex gives rise to two absorption bands at 18.8 and a shoulder at 19.5 kK assignable to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. On the basis of the band positions and magnetic moment values an octahedral configuration is proposed for the complex.

Nickel(II) mono chelate complexes are diamagnetic and show one absorption band a 16.5 kK, presumably indicating a square planar configuration for these two complexes, whereas the base adduct of the nickel(II) *bis* chelate gives rise to three absorption bands at 9.5, 13.8 and 24.4 kK

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TABLE 1—ANALYTICAL DATA OF MIXED LIGAND COMPLEXES

	Compound	Colour	ΛM mhos cm²	Analysis % C Found (Calcd.)	Analysis % H Found (Calcd.)	Analysis % N Found (Calcd.)	μ_{eff} B.M.
1.	CoLClQ	Blue	10.5	57.85 (57.99)	4.01 (4.30)	3.56 (3.76)	4.5
2.	$CoL(NO_3)Q$	Blue	8.4	54.19 (54.14)	4.18 (4.01)	6.82 (7.02)	4.6
3.	CoL_2Q_2	Pink	11.6	70.02 (70.25)	5.38 (5.20)	4.31 (4.55)	5.0
4.	NiLClQ	Red	10.2	58.24 (58.03)	4.06 (4.30)	3.65 (3.76)	Diamag.
5.	$NiL(NO_3)Q$	Red	8.8	54.25 (54.17	4.22 (4.01)	6.84 (7.02)	Diamag.
6.	NiL_2Q_2	Green	6.5	70.08 (70.27)	5.26 (5.21)	4.22 (4.55)	3.1
7.	CuLClQ	Brown	10.4	58.22 (58.05)	4.21 (4.30)	3.68 (3.76)	1.82
8	$CuL(NO_3)Q$	Brown	12.5	54.41 (54.2)	4.15 (4.01)	6.76 (7.08)	1.80
9	CuL_2Q	Blue	11.8	65.92 (66.04)	4.98 (5.09)	2.68 (2.85)	1.79
10.	ZnLClQ	White	9.8	57.14 (57.01)	4.11 (4.22)	3.58 (3.69)	—
11.	$ZnL(NO_3)Q$	White	9 9	53.2 (53.28)	3.86 (3.95)	6.81 (6.91)	—
12.	ZnL_2Q	White	7.5	65.66 (65.80)	5.11 (5.07)	2.64 (2.84)	—

L = anion of 2-hydroxy propiophenone, Q = quinoline

TABLE 2—SPECTRAL DATA OF MIXED LIGAND COMPLEXES

Compound No.	Infrared spectra cm⁻¹ $\nu(C=O)$	$\nu(M-O)$	$\nu(M-N)$	$\nu(M-Cl)$	Electronic spectra ν_{max} in kK (ϵ)
1.	1600	440	320	230	16.0(900)
2.	1590	450	325	235	16 1(900)
3	1595	445	330	235	18.8(95), 19.5
4	1600	445	325	240	15.5(55)
5.	1605	440	320	235	15.8(50)
6.	1600	450	330	230	9.5(6), 18 8(14), 24.4(16)
7	1595	460	325	250	17.3(35)
8	1590	455	320	250	17.0(30)
9.	1590	460	335	245	15.5(60)
10.	1600	460	320	245	—
11.	1605	455	325	250	—
12.	1600	450	330	250	—

attributable[8] to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $\rightarrow {}^3T_{1g}(F)$ and $\rightarrow {}^3T_{1g}(P)$ transitions, respectively. Position of spectral bands and magnetic moment value suggest an octahedral configuration for these complexes.

Monochelate complexes of copper(II) give rise to a broad band around 17.3 kK region indicating probably a four coordinated square planar configuration[9] for these complexes. Mono base adducts of the *bis* chelate of copper(II) also give rise to one broad band at 15.5 kK. On comparison with the spectra of *bis* chelate the band has shifted slightly to low frequency region and there is an increase in intensity of the absorption band. Hence the complex may be presumed to be penta-coordinated on the basis of earlier observations[10-12] on the mono base adducts of β-diketonato complexes of copper(II).

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Infrared Spectra and Thermal Studies of Some Reported Heteropoly Complexes

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IN this short communication thermal behaviour and infrared spectral analysis of five different heteropoly complexes namely, ammonium-12 heteropoly vanadomolybdate, $(NH_4)_{10}[MoV_{12}O_{40}]20H_2O$, ammonium-6 heteropoly vanadotungstate, $(NH_4)_8[WV_6O_{19}]11H_2O$, potassium-6 heteropoly vanadomolybdate, $K_8[MoV_6O_{19}]11H_2O$, ammonium-10 heteropoly vanadocobaltate, $(NH_4)_4[CoV_{10}V_{28}]$-$18H_2O$ and ammonium-12 heteropoly vanadoantimonate, $(NH_4)_7[SbV_{12}O_{36}]24H_2O$ have been discussed.

The compounds have been synthesised and analysed as reported earlier[1-4]. Thermal stability studies on the heteropoly compounds prepared were conducted[5,6] by thermogravimetric analysis (tga), differential thermal analysis (dta) and by heating at fixed temperatures followed by solubility determinations of the heated materials to ascertain decomposition. All dta and tga experiments were done at a heating rate of 5°/min. The heating at fixed temperatures was performed in air in a muffle furnace. To ascertain decomposition due to heating, the heated sample (2-3 g) was placed in 50 ml of water and stirred for 0.5 hr. Degree of insolubility of sample was taken as measure of stability. The weight loss employed to calculate the amount of water or ammonia lost was based on static heating experiments rather than tga results The former were considered to be more accurate since larger samples weighing 2 to 3 g were taken. Complete analysis of the compound was carried out after the decomposition temperature to ascertain the final decomposition of the compounds into the lower oxides of the constituent atoms All tga data on heteropoly vanadates and heteropoly molybdates show weight loss above 650° but this corresponds to slow volatilization of vanadium pentoxide and molybdenum trioxide, respectively.

Ammonium-12 vanadomolybdate is stable at 300° as is shown by its complete solubility in water. The dta data for this hydrate show unresolved endotherms from 25 to 245°. This correlates well with the tga data where the bulk of water as well as ammonia is lost upto this point. From thereon, the compound slowly decomposes by losing water or ammonia. At 350°, the compound is partly stable but the change is complete at 400° where the heteropoly complex breaks completely by losing 4 moles of water (or ammonia). Breakage of the heteropoly cage is confirmed by chemical analysis as well as the dta data which show exotherms at 400-420°.

Ammonium-6 vanadotungstate looses all its water of hydration and ammonia till 300°. The heteropoly cage $[WV_6O_{19}]^{8-}$ is stable at this temperature as it is completely soluble in water. This heteropoly complex breaks at 350° as is shown by its complete insolubility in water. DTA data corroborate the above result. Thermal stability of potassium-6 vanadomolybdate tallies closely with ammonium-6 vanadotungstate.

Ammonium-10 vanadocobaltate loses bulk of its water and ammonia till 200°. The static heating experiments for this salt show a loss of 20%. The tga results show a loss of 19.9% between 25 and 200°, the theoretical being 20.3% corresponding to the loss of 16 molecules of water or ammonia. Between 200 and 400° there is a plateau in the tga showing little loss of weight. A sudden break in tga curve near 400° shows a loss of 7.5% against the theoretical loss of 7.9% corresponding to the loss of 6 molecules of water or ammonia. The heteropoly complex also breaks at 400° as confirmed by dta data showing exotherms at 390-415°.

Ammonium-12 vanadoantimonate looses all its water of hydration as well as ammonia till 400° and it breaks at 450°. So, the thermal stability of the heteropoly cage $[SbV_{12}O_{36}]^{7-}$ is 400°. The ammonium salts can loose ammonia as well as water and thermal analysis alone cannot distinguish this possibility[7].

Infrared spectra of some heteropoly compounds have been examined by Tsigdinos[8], Brown[9] and Sharpless *et al*[10]. Infrared spectra of the above mentioned heteropoly compounds in KBr pellets have been recorded from 4000 to 400 cm^{-1} on a grating IR spectrophotometer, Perkin-Elmer Model 577. Results are given in Table 1. The peaks at 3500-3300 and 3180-3130 cm^{-1} region (antisymmetric and symmetric O–H stretching mode[11]) correspond to those of water[12]. The peaks at 1620-1600 cm^{-1} are also attributed to water (H–O–H bending mode[12]). Lattice water also absorbs in the lower frequency region (600-300 cm^{-1}) owing to liberational modes[12,13]. The sharp peaks at 1420-1390 cm^{-1} may be attributed to the presence of N–H bond[14]. Deformative frequency of the ammonium ion is also known to be active in 3300-3100 cm^{-1} region. So, the broad bands shown by these compounds in the 3500-3100 cm^{-1} region may be due to lattice water as well as ammonium ion. Probable assignments[15-17] for other peaks are 1000-900 cm^{-1} (sharp) for M–O and 800-750 cm^{-1} due to M–O–M bridging (M=V, Mo or W). In the case of interacted heteropoly complexes of V, Mo and W, the absorption due to central metal octahedron may be masked by the absorption of metal oxygen linkage of the surrounding metal octahedra. Absorption due to Co–O linkage has been reported[18] in the lower frequency region 450-430 cm^{-1}. So, in the case of $(NH_4)_4$-$[CoV_{10}O_{28}]18H_2O$, the broad band at 442 cm^{-1} may be due to Co–O absorption of the central octahedron as well as lattice water. Sb–O absorbs below 400 cm^{-1} and therefore could not be observed in the ir. Infrared spectra of the ignited

TABLE 1—INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF HETEROPOLY COMPOUNDS

$(NH_4)_{10}[MoV_{12}O_{38}]20H_2O$	3430b 3140b	1615m	1400s	985s 915s	800s 715s	560s 410m
Ignited sample (400°)	—	—	—	910s 890s		
$(NH_4)_7[WV_5O_{19}]11H_2O$	3445b 3170b	1605b	1405b	975s 930s	840b 755m	600s 410s
Ignited sample (850°)	—	—	—	910s 940s		
$K_7[MoV_5O_{19}]11H_2O$	3440s	1610m		940s	805s 720s	580s
Ignited sample (350°)	—	—	—	910s		
$(NH_4)_4[CoV_{10}O_{28}]18H_2O$	3180b	1615m	1410m	960s	850b 780b	600b 442b
Ignited sample (400°)	—	—	—	930	—	442s
$(NH_4)_7[SbV_{12}O_{36}]28H_2O$	3435b 3175b		1390s	1000s 975s	745s	600s 455m
Ignited sample (450°)	—		—	915s 945s	—	—

s=sharp, m=medium, b=broad.

samples were also taken. The decomposition temperature of the heteropoly complexes was taken as the ignition temperature The peaks, characteristic of lattice water as well as ammonium ion were not found. The observed peaks confirmed the breakage of heteropoly complexes into the lower oxides of their constituent atoms.

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Potential Local Anaesthetic Agents. Part-III · Alkylarylaminoacetyl-2-aminothiazoles and Benzimidazoles

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THE essential structural requirements for anaesthesiophore group in local anaesthetics seems to be a lipophilic moiety containing an aromatic nucleus, an intermediate alkyl or aryl substituted chain and a hydrophilic end consisting of a tertiary amino group[1-4]. The thiazole and imidazole groups are of great importance in biological systems[5-10]. The title compounds appear to possess all the necessary structural requirements for local anaesthetic agent. Therefore, it was thought worthwhile to synthesise some alkylarylaminoacetyl-2-aminothiazoles and benzimidazoles by the condensation of chloroacetylchloride with 2-aminothiazole/benzimidazole followed by treatment with various primary and secondary amines.

The structures of these compounds have been established on the basis of their analysis and infrared spectrum. IR spectra of these compounds show characteristic strong absorption peaks at 1650-1625 cm^{-1} and 1370-1360 cm^{-1} corresponding to C=O and C–N bands, respectively. An

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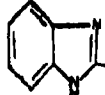
absorption band at 3200-3150 cm^{-1} indicates the NH stretching frequency. A strong absorption peak in the region 1700-1670 cm^{-1} is attributed to secondary amide band.

Experimental

Chloroacetyl-2-aminothiazole/benzimidazole were prepared by known methods[8].

Preparation of dimethylaminoacetyl-2-aminothiazole / N-methylanilinoacetyl-2-aminobenzimidazole : Equimolar quantities of dimethylamine/N-methylaniline and chloroacetyl-2-aminothiazole/chloroacetyl-2-aminobenzimidazole in ethanol were mixed together with constant stirring. After the addition, the reaction mixture was refluxed for 6 hr and the excess of ethanol was distilled off. Residue, on washing with sodium bicarbonate and crystallisation from dilute ethanol afforded the title compounds. The homogenity of these compounds were tested by tlc studies. The percentage yield and melting point of the compounds are reported in Table 1.

These bases were converted into the corresponding hydrochlorides by passing dry hydrogen chloride gas in ethereal solution.

Adopting a similar procedure, various alkylarylamine acetyl-2-aminothiazoles and benzimidazoles have been prepared by the condensation of chloroacetyl-2-aminothiazole/chloroacetyl-2-aminobenzimidazole with different amines.

Biological screening results : The compounds prepared were investigated for their local anaesthetic activity—surface anaesthesia in rabbit cornea[11], infiltration anaesthesia in guineapig[12] and conduction anaesthesia[13] on frog (*Rana tigrina*). The results of preliminary studies are recorded in Table 2. Procaine hydrochloride was used as the standard drug. The screening results indicate that all the compounds except compounds no. 2, 6, 10 and 14 were moderately active when tested as surface anaesthetic at concentration 2 to 2.5% in 0.7% saline. However, compounds no. 1, 4, 5, 11, 13 and 14 were found to be inactive when tested as infiltration anaesthetic at the same concentration, whereas compounds no. 17 and 18 showed

TABLE 1—ALKYLARYLAMINOACETYL-2-AMINOTHIAZOLES AND ALKYLARYLAMINOACETYL-2-AMINOBENZIMIDAZOLES

$$X\text{-}NHCOCH_2\text{-}N\langle^{R_1 \text{ (or H)}}_{R_2}$$

Sl. No.	Compounds* X	R₁ (or H) R₂	Yield %	m.p. °C	Formula	Hydrochloride m.p. °C
1.	(thiazol-2-yl)	Diallyl	75	130	$C_{11}H_{15}N_3OS$	215-17
2.	,,	Dimethyl	70	183	$C_7H_{11}N_3OS$	189-91
3.	,,	Diisopropyl	65	118	$C_{11}H_{19}N_3OS$	185-87
4	,,	N-methylanilino	70	90	$C_{12}H_{13}N_3OS$	213-15
5.	,,	Pyridyl	75	106	$C_{10}H_{10}N_4OS$	221-22
6.	,,	Pyrimidino	60	135	$C_9H_9N_5OS$	192-94
7	,,	N,N-dimethyl anilino-p-	75	82	$C_{13}H_{16}N_4OS$	201-03
8.	,,	Piperidino	70	87	$C_{10}H_{15}N_3OS$	224-26
9.	,,	Piperizino	68	65	$C_9H_{14}N_4OS$	205-07
10	,,	Morpholino	60	70	$C_9H_{13}N_3O_2S$	195-97
11.	(benzimidazol-2-yl)	Diallyl	80	120	$C_{15}H_{18}N_4O$	185-87
12.	,,	Dimethyl	75	125	$C_{11}H_{14}N_4O$	241-42
13.	,,	Diisopropyl	68	107	$C_{15}H_{22}N_4O$	233-35
14.	,,	N-methylaniline	65	98	$C_{16}H_{16}N_4O$	197-99
15	,,	Pyridyl	76	92	$C_{14}H_{13}N_5O$	203-05
16	,,	Pyrimidino	60	85	$C_{13}H_{12}N_6O$	217-19
17.	,,	N,N-dimethyl-anilino-p-	68	101	$C_{17}H_{19}N_5O$	235-37
18.	,,	Piperidino	70	135	$C_{14}H_{18}N_4O$	176-77
19.	,,	Piperizino	75	117	$C_{13}H_{17}N_5O$	187-89
20.	,,	Morpholino	62	79	$C_{13}H_{16}N_4O_2$	179-81

* Elemental analyses results for C, H, N and S for these compounds are within ±0.5% of the theoretical values.

TABLE 2—BIOLOGICAL SCREENING RESULTS OF ALKYLARYLAMINOACETYL-2-AMINOTHIAZOLES AND ALKYLARYLAMINOACETYL-2-AMINOBENZIMIDAZOLES AS LOCAL ANAESTHETIC

Compound No.	Surface anaesthesia			Infiltration anaesthesia			Conduction anaesthesia			
	Conc. of drug (%)	Intensity	Duration (min)	Conc. of drug (%)	Intensity	Duration (min)	Conc. of drug (%)	Onset of anaesthesia (min) in HCl of stength		
								0 5 N	0.1 N	0.2 N
1.	2	complete	3	0.2	nil	–	0 2	20	21	21
2.	2	nil	–	0 2	partial	8	–	–	–	–
	–	–	–	–	complete	10	0.2	18	19	19
3.	2	partial	8	0.2	complete	15	0.2	8	9	10
	2 5	complete	10	–	–	–	–	–	–	–
4.	2	complete	14	0 2	nil	–	0.2	15	16	17
5.	2	partial	6	0 2	nil	–	0 2	20	20	21
	2 5	complete	8	–	–	–	–	–	–	–
6	2	nil	–	0 2	complete	9	0.2	23	24	24
7.	2	complete	22	0.2	complete	16	0.2	9	10	10
8	2	complete	18	0.2	partial	5	0.2	13	15	16
	–	–	–	0.25	complete	7	–	–	–	–
9	2	partial	12	0 2	complete	12	0 2	10	11	12
	2.5	complete	14	–	–	–	–	–	–	–
10	2	nil	–	0.2	complete	8	0 2	5	6	7
11	2	complete	4	0.2	nil	–	0 2	17	18	19
12	2	partial	4	0.2	complete	3	0.2	20	22	22
	2.5	complete	5	–	–	–	–	–	–	–
13	2	complete	7	0.2	nil	–	0.2	9	10	10
14	2	nil	–	0.1	nil	–	0 2	19	20	20
	–	–	–	0.2	nil	–	–	–	–	–
15.	2	partial	2	0 1	partial	4	0.2	27	29	29
	2.5	complete	4	0.2	complete	6	–	–	–	–
16	2	complete	8	0 2	complete	5	0.2	31	32	33
17	2	complete	20	0.2	complete	37	0 2	7	8	8
18	2	complete	19	0 2	complete	20	0 2	10	11	12
19	2	partial	13	0.1	partial	10	0.2	12	13	13
	2 5	complete	15	0 2	complete	12	–	–	–	–
20	2	complete	10	0 2	complete	10	0 2	16	17	17
Procaine hydrochloride (Standard)	2	complete	15	0.2	complete	12	0 2	15	16	17

maximum activity with duration of infiltration anaesthesia on frog. Compounds no 7, 8, 17 and 18 were found to be more active than the standard drug when tested as surface anaesthetic. In comparison to the standard drug, the compounds no. 4 and 20 were found to be equally active, compounds no. 1, 2, 5, 6, 11, 12 and 14 slightly more active and compounds no. 15 and 16 were observed to be most active.

Acknowledgement

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Studies on Antitubercular Agents. Part-III : Preparation of Some p-(2,4-Diarylamino-6-S-Triazinylamino)-Benzaldehyde/Acetophenone Thiosemicarbazones as Potential Tuberculostatic Agents

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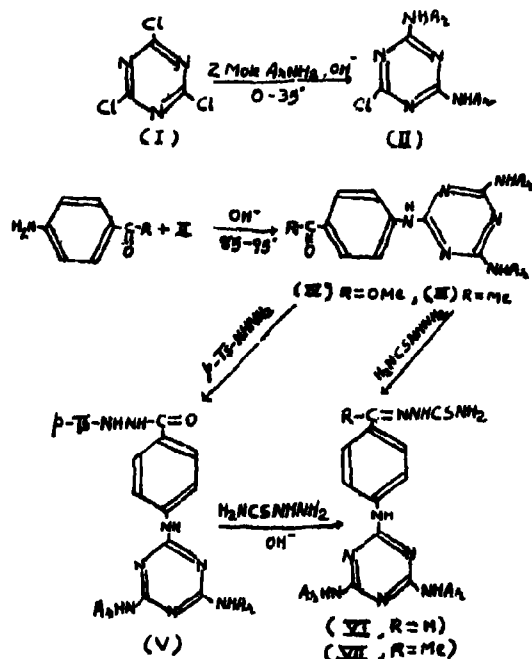
LITERATURE reveals that a number of studies have been carried out on the antileprotic and antitubercular activity of thiosemicarba-

zones[1-8,17,18]. The thiosemicarbazones of aromatic aldehydes in general possess potential drug activity. The study of structure-activity relationship suggests that the presence of substituent in benzene ring increases the *in vitro* tuberculostatic activity but only *p*-substituted benzaldehyde thiosemicarbazones have significant *in vivo* activity[9-16]. Further, s-triazine derivatives have wide spectrum of biological activity[19-27]. It was therefore thought that incorporation of 2,4-diarylamino-6-s-triazinyl moiety into *p*-aminobenzaldehyde/acetophenone thiosemicarbazones might modify their tuberculostatic activity.

The synthetic sequence of the title compounds is outlined in Scheme 1.

Scheme 1

Experimental

Preparation of 2,4-diarylamino-6-chloro-s-triazine(II) : These were prepared by reported method[19-21].

Preparation of p-*(2,4-diarylamino-6-*s*-triazinyl-amino)-acetophenone* (III) : To a solution of *p*-aminoacetophenone (0.01 mole) in dioxane (10 ml) was added a solution of appropriate II (0.01 mole) in dioxane (15 ml) at 80°. The solution heated at 85-90° for 2 hr with the simultaneous addition of NaOH (aqueous 10% ; 4 ml) and poured on water, filtered, washed with water, dried and recrystallised from ethanol (95%).

Preparation of 2,4-diarylamino-6-(4-carbomethoxyanilino)-s-triazine(IV) : Methyl-*p*-aminobenzoate (0.015 mole) and appropriate II (0.015 mole) were separately dissolved in dioxane (25 ml) and mixed at 80°. The solution refluxed for 2 hr with the simultaneous dropwise addition of NaOH (aqueous 10% ; 6 ml), the contents poured on ice, filtered, washed repeatedly with water and recrystallised from ethanol (95%).

Preparation of p-*(2,4-diarylamino-6-s-triazinyl-amino)-benzoyl* p-*toluenesulfonyl hydrazide* (V) : The ethanolic solution of IV (0.012 mole) and *p*-toluenesulfonylhydrazide (0.0122 mole) was refluxed for 3.5 hr and allowed to cool to room temperature (25°) and filtered. The product so obtained was washed with boiling water and recrystallised from ethanol (95%). The ir spectra of V show strong bands in the 1180-1150, 1340-1305 cm^{-1} regions.

Preparation of p-*(2,4-diarylamino-6-s-triazinyl-amino)-benzaldehyde thiosemicarbazone* (VI)[28] : Thiosemicarbazide (0.01 mole) and appropriate V (0.008 mole) were dissolved in a mixture of ethylene glycol and water (3 : 1) containing NaOH (10% ; 10 ml). The solution heated at 90-95° for 2.5 hr and poured on ice, rendered acidic with 1 *N* HCl, filtered, washed with water and recrystallised from ethanol (95%).

Preparation of p-*(2,4-diarylamino-6-s-triazinyl-amino)-acetophenone thiosemicarbazones*(VII) : Usual condensation of thiosemicarbazide and III in EtOH furnished VII which were recrystallised from ethanol (95%).

The physical data of the compounds are recorded in Tables 1 and 2. The ir spectra of VI and VII show strong bands in the 1660-1630, 1500-1470, 1380-1360 and 1220-1205 cm^{-1} regions.

Antimycobacterial activity : The antimycobacterial activity of the compounds was studied *in vitro* by two fold serial dilution method against $H_{37}R_v$ strain of *Mycobacterium tuberculosis* using Lowenstein-Jensen's egg medium. MIC (Table 2)

TABLE 1—PHYSICAL DATA OF THE 2,4-DIARYLAMINO-6-CHLORO/SUBSTITUTED ANILINO-s-TRIAZINES (II, III, IV AND V)

Ar	Type of compound	% Yield	m.p. °C	Type of compound	% Yield	m.p. °C
Phenyl	II	88.7	197[20]	IV	97.6	184
p-Tolyl	II	93.1	197[20]	IV	99.1	202
p-Anisyl	II	93 4	202[21]	IV	96.0	205
p-Chlorophenyl	II	90.9	222-23[21]	IV	98.4	194
p-Bromophenyl	II	94 6	240-41	IV	96.5	199
p-Nitrophenyl	II	94 7	304[20]	IV	95.6	222-23
m-Chlorophenyl	II	92.2	296-97	IV	97.0	214
m-Tolyl	II	93 4	144[20]	IV	98.6	198
o-Tolyl	II	90.9	164[20]	IV	97.5	198
o-Tolyl	III	97.2	209	V	50.7	293
m-Tolyl	III	95 1	214	V	54.0	296
m-Chlorophenyl	III	90.8	263	V	44.1	284
p-Nitrophenyl	III	93.2	298	V	43.9	335(d)
p-Bromophenyl	III	94.6	273	V	47.7	281
p-Chlorophenyl	III	93.1	238	V	49.6	293
p-Anisyl	III	96.9	242	V	57.2	304
p-Tolyl	III	95.1	214	V	56.2	287
Phenyl	III	96.5	216	V	55.0	298

All the above compounds gave satisfactory C, N and S analyses.

TABLE 2—DATA OF THE THIOSEMICARBAZONES VI AND VII

Ar	R	% Yield	m.p. °C	MIC μg/ml
C_6H_5-	H	48 4	236	8
C_6H_5-	CH_3	66 6	311	64
p-$CH_3-C_6H_4-$	H	48 7	231	8
p-$CH_3-C_6H_4-$	CH_3	68.3	298	64
p-$CH_3O-C_6H_4-$	H	48 2	248	8
p-$CH_3O-C_6H_4-$	CH_3	78 2	265	64
p-$Cl-C_6H_4-$	H	48 1	238	8
p-$Cl-C_6H_4-$	CH_3	76 9	275	64
p-$Br-C_6H_4$	H	42 1	298(d)	16
p-$Br-C_6H_4-$	CH_3	77 1	302	–
p-$NO_2-C_6H_4-$	H	42 6	245	–
p-$NO_2-C_6H_4-$	CH_3	77 6	336	–
m-$Cl-C_6H_4-$	H	49 8	219-20	8
m-$Cl-C_6H_4-$	CH_3	74 9	283	32
m-$H_3C-C_6H_4-$	H	48.0	230-31	8
m-$H_3C-C_6H_4-$	CH_3	66.5	294	32
o-$H_3C-C_6H_4-$	H	50 7	238	8
o-$H_3C-C_6H_4-$	CH_3	69 3	288	32

All the above compounds gave satisfactory C, N and S analyses.

is the minimum concentration which inhibits almost completely the growth of the test bacterium.

It is evident from the experimental data (Table 2) that p-(2,4-diarylamino-6-s-triazinylamino)-benzaldehyde thiosemicarbazones (VI) have higher tuberculostatic activity than the corresponding acetophenone thiosemicarbazone analogues (VII). The intermediate compounds II-V do not possess any significant activity against *Mycobacterium tuberculosis* reflecting on the key role of thiosemicarbazone moiety in the antimycobacterial activity of the title compounds.

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Studies on Antitubercular Agents. Preparation of 2-Arylamino-4-(4-Carbethoxyanilino)-6-Isonicotinylhydrazino-1,3,5-Triazine

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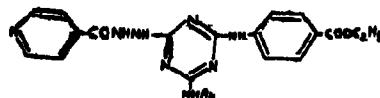
LITERATURE reveals that a number of studies has been carried out on the chemotherapeutic potentialities of 1, 3, 5-triazine derivatives. It was thought that incorporation of substituted amino-1,3,5-triazine moiety into the tuberculostatic agent isonicotinic acid hydrazide, might modify the biological activities. Thus, 2,4,6-trichloro-1,3,5-triazine and ethyl p-aminobenzoate were reacted to produce 2-(4-carbethoxyanilino)-4,6-dichloro-1,3,5-triazine, which on reaction with isonicotinic acid hydrazide and subsequently with different aromatic amines gave 2-arylamino-4-(4-carbethoxyanilino)-6-isonicotinylhydrazino-1,3,5-triazine[1-4].

2-arylamino-4-(4-carbethoxyanilino)-6-isonicotinylhydrazino-1,3,5-triazine.

Experimental

Preparation of 2-(4-carbethoxyanilino)-4,6-dichloro-1,3,5-triazine : 2,4,6-Trichloro-1,3,5-triazine (0.01 mole) and ethyl p-aminobenzoate (0.01 mole) were separately dissolved in acetone (100 ml) and mixed at 0°. To it, NaOH (aqueous 4% ; 100 ml) was added dropwise and mechanically stirred at 0-5°. The contents poured on ice, titrated with HCl (5 *N*), filtered and crystallised from THF, m.p. 284° (reported m.p. 282-87°). (Found : C, 50.40 ; Cl, 24.8 ; N, 19 25. $C_{12}H_{10}Cl_2N_4O_2$ requires C, 51.25 ; Cl, 25.27 ; N, 19.97%).

Preparation of 2-(4-carbethoxyanilino)-4-chloro-6-isonicotinylhydrazino-1,3,5-triazine : Isonicotinic acid hydrazide (INH, 0.08 mole) and 2-(4-carbethoxyanilino)-4,6-dichloro-1,3,5-triazine (0.08 mole) were dissolved in dioxane at 10 to 15°, followed by dropwise addition of $NaHCO_3$ (1 *M* ; 90 ml) and stirring at 30-35° for 3 hr. The product isolated and crystallised from ethanol (95%), m.p. 325°. (Found : C, 56.22 ; H, 3.91 , N, 24.38. $C_{18}H_{16}ClN_7O_3$ requires C, 55 89 ; H, 4.14 ; N, 25.36%).

Preparation of 2-arylamino-4-(4-carbethoxyanilino)-6-isonicotinylhydrazino-1,3,5-triazine : Amine (0.002 mole) and 2-(4-carbethoxyanilino)-4-chloro-6-isonicotinylhydrazino-1,3,5-triazine were taken in dioxane and the solution refluxed for 2 hr with the simultaneous dropwise addition of aqueous $NaHCO_3$ (10% ; 2 ml). The solution was cooled, poured on ice, filtered, washed with water and crystallised from ethanol (95%) in 80 to 85% yields.

Antimycobacterial screening : The *in vitro* antitubercular activity of the hitherto synthesised 2-arylamino-4-(4-carbethoxyanilino)-6-isonicotinylhydrazino-1,3-5-triazine have been studied at 25 μg/ml concentration (solvent - acetone) against $H_{37}R_v$ strain of *Mycobacterium tuberculosis* using Lowenstein-Jensen medium. The procedure was duplicated with solvent for control purposes.

Table 1—Data of the 2-Arylamino-4-(4-Carbethoxyanilino)-6-Isonicotinylhydrazino)-1,3,5-Triazine

Sl. No.	Ar	m.p °C	Activity against $H_{37}R_v$ strain of *M. tuberculosis*
1	Phenyl	150	+
2.	o-Chlorophenyl	218	+
3.	o-Tolyl	231	+
4.	o-Carboxyphenyl	223	+
5.	*m*-Chlorophenyl	204	+
6.	*m*-Tolyl	231	+
7.	*m*-Nitrophenyl	246	+
8.	*p*-Chlorophenyl	165	+
9	*p*-Tolyl	180	+
10.	*p*-Anisyl	171	+
11.	*p*-Nitrophenyl	190	+
12	*p*-Bromophenyl	223	+

All the above compounds gave satisfactory C, H and N analysis.

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Synthesis of Some New 1-Substituted 5-bromo-3-aryloxy acetyl hydrazono-2-indolinones as Potential Antibacterial Agents

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SEVERAL isatin analogous have been reported to possess antibacterial[1], antiviral[2], anthelmintic[3], herbicidal[4] and fungicidal[5] properties. In addition to this, cysticidal[6] and hypotensive[7] responses have also been reported in certain isatin derivatives. Furthermore, tuberculostatic responses[8] of aryloxy acetyl hydrazides are also well established.

Encouraged by these findings, 5-bromoisatin was condensed with *p*-substituted phenoxy acetyl hydrazides to furnish 5-bromo-3-aryloxy acetyl hydrazono-2-indolinones (I). Similarly, 5-bromo-1-methyl isatin gave 1-methyl-5-bromo-3-(*p*-substituted)-phenoxy acetyl hydrazono-2-indolinones. When compounds (I) were subjected to Mannich reaction, 1-aminomethyl-5-bromo-3-(*p*-substituted)-phenoxy acetyl hydrazono-2-indolinones were obtained and their antibacterial activity were tested.

Experimental

Melting points were taken in open capillaries and are uncorrected. All the compounds were characterised by ir spectroscopy, recorded on Perkin-Elmer 137 IR spectrometer in KBr and the λ_{max} values are expressed in cm^{-1}. The purity of the compounds was checked by tlc on silica gel-G plates and the spots were located by I_2 vapours.

Synthesis of 5-bromoisatin (I) : The 5-bromoisatin was prepared following the literature method[9,10].

N-Methylation of isatin (II) : This was performed by the procedure described by Harley-Manson *et al*[11].

Aryloxy acetyl hydrazides (III-VII) : Hydrazide derivatives of substituted phenols were prepared by the method of Yale *et al*[13].

3-Phenoxy acetyl hydrazono-2-indolinone (VIII) : A mixture of 5-bromoisatin (4.4 g ; 0.02 mole) and phenoxy acetyl hydrazide (3.3 g; 0.02 mole) in ethanol (25 ml) containing a few drops of glacial acetic acid was refluxed on a water bath for 2 hr The reaction mixture was then allowed to cool to room temperature. The solid mass thus separated was filtered off, washed with cold ethanol and recrystallised from ethyl acetate

IR : 3200 (N—H stretch, broad peak with shoulder), 1720 (C=O stretch shoulder at 1680 for non-cyclic C=O stretch) and 1620 cm^{-1} (C=N), etc.

All the other compounds of the series (IX-XII) were synthesised in a similar manner and their relevant data are given in Table 1.

1-Methyl-5-bromo-3-phenoxy acetyl hydrazono-2-indolinone (XIII) : This was prepared by heating a mixture of 1-methyl-5-bromo isatin (1.2 g ; 0.1 mole) and phenoxy acetyl hydrazide (0.83 g ; 0.1 mole) in ethanol (25 ml) containing a few drops of glacial acetic acid for 4 hr on a water bath. The reaction mixture was cooled and the solid product thus separated was recrystallised from $CHCl_3$

IR : 3150 (N–H stretch), 2900 (C–H stretch aliphatic), 1720 (C=O stretch cyclic), 1675 (C=O stretch non-cyclic) and 1610 cm^{-1} (C=N), etc.

Other compounds of this series (XIV-XVII) were also synthesised by the similar method (Table 1).

1-Morpholinomethyl-5-bromo-3-phenoxyacetyl hydrazono-2-indolinone (XVIII) : The compound 5-bromo-3-phenoxy acetyl hydrazono-2-indolinone (1.24 g ; 0.01 mole) was suspended in ethanol (15 ml). To this suspension was added 37% formalin (0.1 ml) and morpholine (0.2 ml ; 0.01 mole) with vigorous stirring. This mixture was then heated on water bath for 10 min and allowed to stand overnight at room temperature. The separated product was filtered and washed with petroleum ether (60-80°) and air dried. Finally, it was recrystallised from $CHCl_3$-petroleum ether.

IR : 3200 (N–H stretch), 2850 (C–H stretch aliphatic), 1720 (C=O stretch cyclic), 1675 (C=O stretch non-cyclic), and 1610 cm^{-1} (C=N), etc.

Similarly, compounds (XIX-XXVII) were also synthesised (Table 1).

Antibacterial activity : The method of agar diffusion technique[13,14] was employed for determining antibacterial activity of all the compounds. The test organisms included *Bacillus cereus*, *Staphylococcus aureus* and *Bacillus pumilus*. Sterile filter paper discs (diameter 5 mm) saturated with the solution of the test compound (10 mg/ml in ethanol) were placed on nutrient agar plates [1.5% (w/v) agar, 5% (w/v) NaCl, 0.5% (w/v) glucose and 3.5% (w/v) peptone ; *p*H 6.8-7.0], after drying up of the solvent. The plates were incubated at 37° for 24 hr. Inhibition zones around the discs were measured. Tests were carried out in triplicate and the results are recorded in Table 1.

TABLE 1—PHYSICAL CONSTANTS AND ANTIBACTERIAL ACTIVITY OF 1-SUBSTITUTED-5-BROMO-3-ARYLOXY ACETYL HYDRAZONO-2-INDOLINONES (VIII-XXVII)

Compd. No.	R	R′	m.p. °C	Antibacterial activity Mean inhibition area after 24 hr *B. cereus*	*S. aureus*	*B. pumilus*
VIII	H	H	280	++	++	++
IX	H	Cl	242	++	+	–
X	H	CH_3	272	+	+	+
XI	H	OCH_3	238	+	–	+
XII	H	Br	252	–	+	–
XIII	CH_3	H	212	–	+	+
XIV	CH_3	Cl	202	+	–	+
XV	CH_3	CH_3	218	–	–	–
XVI	CH_3	OCH_3	188	–	–	–
XVII	CH_3	Br	192	–	–	–
XVIII	morpholino methyl	H	152	+++	++	++
XIX	,,	Cl	189	+	+	+
XX	,,	CH_3	146	+	–	+
XXI	,,	OCH_3	147	+	–	–
XXII	,,	Br	178	–	+	–
XXIII	piperidino methyl	H	158	+	–	+
XXIV	,,	Cl	176	–	+	+
XXV	,,	CH_3	184	+	+	+
XXVI	,,	OCH_3	155	+	–	–
XXVII	,,	Br	164	–	–	–

Elemental analysis of C, H and N were found within limits.
Yields of all the compounds ranged between 60-80%.
(–)=No inhibition, (+)=Zone size 6-8 mm, (++)=Zone size 8-12 mm, (+++)=Zone size >12 mm.

Discussion

Compounds no 8 and 18 were found to be the most active against all the microorganisms tested, whereas compound no. 9 was found to be active only against *B. cereus* Rest of the compounds were moderately active.

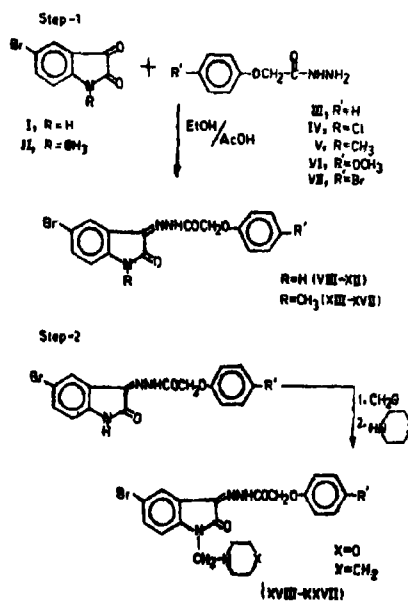
Step-1

I, R=H
II, R=CH_3
EtOH/AcOH
III, R′=H
IV, R′=Cl
V, R′=CH_3
VI, R′=OCH_3
VII, R′=Br

R=H (VIII-XII)
R=CH_3 (XIII-XVII)

Step-2

1. CH_2O
2. HN◯

X=O
X=CH_2
(XVIII-XXVII)

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Synthesis of Substituted 6-Pyrazolo and 6-Isoxazolo-Benzoxazoles and Their Physiological Activity

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A wide range of physiological properties are found to be associated with benzoxazoles, isoxazoles and pyrazoles. Heterocycles, substituted with hydroxyphenyl moiety, have been used as analgesic[1], antitissuive[2] and anticonvulsant[3] agents. A number of hydroxyaryl pyrazoles were found to possess marked antifungal activity[4]. The present investigation is aimed at a study of antifungal activity of some substituted isoxazolobenzoxazoles and pyrazolobenzoxazoles and a series of the above new compounds are synthesised and screened for antifungal and antibacterial activities.

Chromones in their reactions with hydrazine or phenylhydrazine behave like α,β-unsaturated ketones and undergo Michael addition. The nucleophile attacks at C-2 with concomitant opening of the pyrone ring. The intermediates thus formed undergo cyclisation to give 3(5)-*o*-hydroxyphenyl-pyrazole system[5,6].
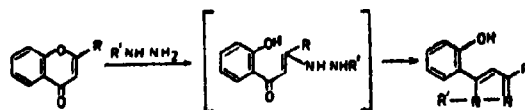
Chart 1. R = alkyl or aryl, R′ = H or ph

In the present investigation, the behaviour of some substituted chromonooxazoles with hydroxylamine, hydrazine and phenylhydrazine is studied. Substituted chromonooxazoles can be prepared starting from *o*-hydroxyaminochromones either by treating with various aldehydes in nitrobenzene[7] or treatment with carboxylic acids in presence of polyphosphoric acid[8].

Chromonooxazoles (I), upon treatment with hydroxylamine hydrochloride in pyridine, underwent the cleavage of the chromone ring followed by the formation of isoxazole unit, resulting in the formation of II. The same chromonooxazole (I), when treated with hydrazinehydrate or phenylhydrazine in alcohol medium yielded III (Chart 2). These results are in accordance with Ghosh *et al*[9].
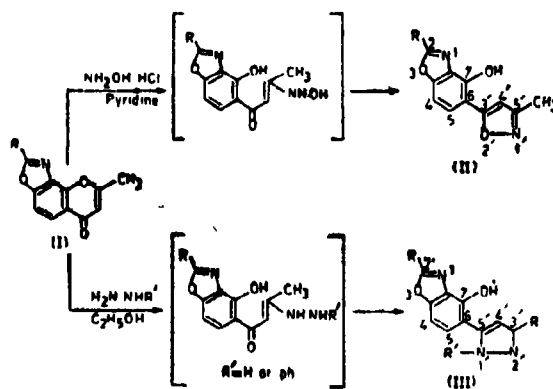
Chart 2

All the products gave green colouration with neutral ferric chloride, pink colour with conc. sulphuric acid and dark violet colour with titanium(III) chloride. The uv maxima are recorded at 250 ± 10 nm due to benzoxazole chromophore and at 280 ± 10 nm due to extended conjugation. The ir bands at 1570, 1350, 1050 cm^{-1} are characteristic of oxazole ring system. A broad absorption at 3200 cm^{-1} is for chelated hydroxyl group. Further, absorption at 1640 cm^{-1} is indicative of $>C=N$. The pmr results have been included in Table 1.

Physiological activity :

All the above compounds have been tested for antibacterial activity using *Staphylococcus lutea*,

TABLE 1

Sl No	Compound	Assignment					
		3'-CH_3	4'H	4H, 5H	Chelated 7-OH	Substituent at 2	Substituent at N
1.	2-o-Toluyl-6-(5'-methylisoxazole-3'-yl)-7-hydroxybenzoxazole	2.3(s) (5'-Me)	6.6(s)	8.1(m)	10.4 to 10.6 (broad)	2.8(s) Me, 7.2 to 7.6 (m) ar protons	—
2	2-Phenyl-6-(3'-methylpyrazole-5'-yl)-7-hydroxybenzoxazole	2.4(s)	6.6(s)	8.2(m)	10.4 to 10.6 (broad)	7.4 to 7.7(m) ar protons	2.5 (broad) (N H)
3	2-p-Chlorophenyl-6'-(1'-phenyl-3'-methylpyrazole-5'-yl)-7-hydroxybenzoxazole	2.4(s)	6.3(s)	8.2(m)	10.4 to 10.6 (broad)	2.7(s) Me 7.2 to 7.5(m) ar proton (4H	7.2 to 7.5 (m) aromatic (5H)

TABLE 2

Sl No	Compound		m p °C	Yield %	Analysis % Found (Calcd) C	H	N
	2-(R)-6-(5'-Methylisoxazole-3'-yl)-7-hydroxybenzoxazole						
	R						
1	Phenyl		222	76	72.6 (72.8)*	4.3 (4.2)	10.1 (10.0)
2	(p-Chlorophenyl)		224	74	64.7 (64.8)	3.5 (3.4)	8.8 (8.9)
3	(2-Naphthyl)		236	72	73.7 (73.6)	4.1 (4.0)	8.2 (8.1)
4	(3-Pyridyl)		240	68	69.1 (69.3)	3.8 (3.9)	15.3 (15.1)
5	o-Toluyl		192	77	73.3 (73.4)	4.6 (4.7)	9.4 (9.6)
6	p-Toluyl		200	78	73.2 (73.4)	4.5 (4.7)	9.6 (9.5)
	2-(R)-6-(1'-R'-3'-Methylpyrazole-5'-yl)-7-hydroxybenzoxazole						
	R	R'					
1	Phenyl	Phenyl	207	82	75.0 (75.2)	4.9 (4.8)	11.5 (11.4)
2	Phenyl	H	300	80	68.9 (68.8)	4.8 (4.7)	15.2 (15.0)
3	p-Chlorophenyl	Phenyl	232	76	68.6 (68.7)	4.0 (3.9)	10.5 (10.4)
4	2-Naphthyl	Phenyl	272	81	77.5 (77.6)	4.4 (4.5)	10.2 (10.0)
5	6-Methyl-3-coumarinyl	Phenyl	260	79	72.4 (72.3)	3.9 (4.0)	9.4 (9.3)

* Figures in parentheses are calculated values

S. aureus, *Escherichia coli* and *Bacillus magetenum* as representative species, employing glass humid chamber technique. None of the compounds are found to be antibacterial. The antifungal activity has been assessed by employing *Drechslera rostrata* (Drechs) and *Alternatia alternata* (Keissler) as the test organisms. All the compounds tested could inhibit the spore germination at 30 μg/ml up to the maximum level. Hence it is concluded that all the compounds possess high antifungal activity but not antibacterial.

Experimental

All the melting points are uncorrected. IR spectra are recorded on Perkin-Elmer 297 instrument in KBr pellets. NMR is recorded on a Varian A-60 MHz instrument. Micro analysis is done on Hewlett-Packard 185-B Model. The data are given in Table 2

All the chromonooxazoles were prepared by procedures reported earlier[7,8]

2-Substituted-6-(5'-methylisoxazole-3-yl)-7-hydroxybenzoxazoles : The parent chromonooxazole and hydroxylamine hydrochloride were taken in equimolar ratio and dissolved in pyridine, refluxed for 4 hr and excess pyridine removed by distillation. The reaction mixture was poured on crushed ice and neutralised with dilute acetic acid with constant stirring. The resulting solid product was washed thoroughly with cold water and dried. All the compounds were recrystallised from benzene-petroleum ether. Yields were above 80%.

2-Substituted-6-[(1'-substituted-3'-methylpyrozol-5'-yl)]-7-hydroxybenzoxazoles : All the N-phenyl pyrazolyl and pyrazolyl substituted benzoxazoles were prepared by taking equimolar proportions of chromonooxazole and phenylhydrazine or hydrazine hydrate in alcohol and refluxing and working out in the above manner.

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A Field Test for The Detection and Semiquantitative Determination of Sulphurdioxide in Air and Water

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SULPHURDIOXIDE is a major pollutant originating from industrial and domestic emissions. It is also a major component of automobile exhaust and its applications as a preservative or fungicide are major sources of sulphurdioxide pollution. The "Threshold Limit Value" adopted by American Conference of Governmental Industrial Hygienists (1969) is 5 ppm[1]. In view of its hazardous effects on health, vegetation and property[2], a fast and reliable method for detection of traces of sulphurdioxide would be of immense value.

In search of better organic bases to increase the intensity of brick red colouration in the Bodeker reaction[3], it was found that malonyldihydrazide (MDH) along with zinc acetate and sodium nitroprusside gives a very intense brick red precipitate in solution. The reaction is used for spot test to detect as low as 0.2 ppm sulphurdioxide in air or water.

Experimental

Preparation of malonyldihydrazide : Malonyldihydrazide was prepared by adding hydrazine hydrate (0.1 mole in alcohol) to an alcoholic solution of diethyl malonate (0.05 mole in alcohol) in 2 : 1 mole ratio. The white solid obtained was crystallised from water, m.p. 150°.

Reagents : (1) 1 *M* zinc acetate solution in 5% v/v glycerol, (2) 2% w/v solution of sodium nitroprusside in distilled water and (3) 2% w/v solution of malonyldihydrazide in distilled water were used.

Sulphurdioxide for air analysis was prepared from freshly prepared sodium sulphite solution in water with a small amount of HCl

All reagents used were of A. R. grade.

Procedure

Spot test for the detection of sulphurdioxide as sulphite ions in water : 1 ml of each of the above mentioned reagents 1, 2 and 3 were taken in a 10 ml beaker serially. A cream coloured colloidal solution was formed. The solution was stable for a week. One drop of this solution was taken on a spot plate. One drop of sulphurdioxide solution (5 μg/ml) was added to this spot. A brick red precipitate formed immediately which indicated the presence of sulphurdioxide. The precipitate was stable for more than 24 hr.

Detection in air : Test papers were prepared and examined for the detection of traces of sulphurdioxide in air by the earlier reported method[4] using 2% w/v solution of malonyldihydrazide along with 1 *M* zinc acetate solution and 2% sodium nitroprusside solution. The colour produced in the test paper was compared with that obtained from passing 1 litre of air containing 0 1 to 2 ppm of sulphurdioxide. A semiquantitative determination was possible.

Results and Discussion

The present method is more sensitive than the earlier reported methods. Brick red precipitate is not soluble in organic solvents like chloroform, carbon tetrachloride, benzene, butanol, methanol, ethanol, methyl acetate, etc. Precipitate is either decomposed or remains undissolved in these solvents.

Carbonate, chloride, sulphate, ammonia, nitrate, nitrite, phosphate did not interfere in this reaction. Sulphide ion was found to give similar colour reaction. However, the interference from sulphide ion can be eliminated by passing the air sample through mercuric chloride solution.

The pH of the coloured solution after the formation of the precipitate was found to be between 5.5 – 5.8. Increase in intensity of the colour by addition of malonyldihydrazide was supposed to be due to the formation of $[Zn(MDH)_2]_2 Fe(CN)_5 NO.SO_3$. Following the described procedure, semi quantitative determination of sulphites in water is possible by comparing the colour of the precipitate produced by varying amounts of sulphites (0.1 to 2 ppm) with that produced by the unknown Further studies to establish this reported reagent system as an absorbing reagent for sulphurdioxide are being persued

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Spectrophotometric Determination of Aromatic Amines Using Catechol and Iodine

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A new spectrophotometric method for the assay of primary and secondary aromatic amines with catechol-iodine reagent at pH 2.6±0.6 has been developed. It is based on the development of purple-red colour of maximum absorbance (λ_{max} 500-520 nm) within 5-20 min (depending on the amine) after mixing with the reagent. The colour is stable for 2 hr. The method is simple, reproducible and accurate within ± 1.0%. It has been extended to the determination of drugs in pure and dosage forms which either contain a free primary aromatic amino group (sulpha drugs, local anaesthetics, dapsone) or release it through hydrolysis (succinyl sulphathiazole) or reduction (chloramphenicol or folic acid).

Experimental

The absorbance measurements were made with Shimadzu UV 140 double beam spectrophotometer with 1 cm glass cells. The pH of the solution was adjusted to the desired value using an Elico model LI-120 digital pH meter. A freshly prepared 0.1% aqueous solution of catechol was used. Glycine-HCl (pH 1.0-2.1) and potassium acid phthalate-HCl buffers were prepared according to the procedures given by Lurie[1]. All the other reagents used were of analytical grade.

General procedure. To a 25 ml flask, 15 ml of potassium acid phthalate buffer pH 3.1, 1 ml of 0.1% catechol, 1 ml of 0.01 N iodine and 1-5 ml of aromatic amine (concentration range, Table 1) were added in the given order. The solution was then diluted to the mark and allowed to stand at room temperature for 5-30 min (depending on the amine). At the end of this period, the absorbance was read at 500-520 nm against a reagent blank. The aromatic amine concentration was read from a calibration curve prepared with the same compound under identical conditions.

Procedure for compounds which yield primary aromatic amino group on hydrolysis · About 25 mg of the sample was boiled with 20 ml 6 N HCl for 1 hr under reflux, cooled and the excess hydrochloric acid removed under vacuum. The residue was dissolved in 50 ml of warm water and diluted to 250 ml after adjusting the pH to 5.0-7.0. The general procedure was then followed.

Procedure for compounds which yield a primary arylamino group on reduction · About 25 mg of the sample was treated with 25 ml 4 N HCl and 0.75 g zinc dust added in portions. After standing for 1 hr at room temperature, the solution was filtered through cotton wool, the residue was washed with water, excess HCl was removed and diluted to 250 ml after adjusting the pH to 5.0-7.0. The general procedure was then followed.

The sampling and preliminary treatment of dosage forms such as tablets and capsules was performed according to reported procedures[2,3] and the assays were carried out as above depending on the nature of the compound.

Results and Discussion

Absorbance curves : The absorbance curves of reagent, primary arylamines and N-methylaniline show maximum absorbance at 500-520 nm ; whereas catechol-iodine or primary arylamine-iodine show practically no absorption The maximum intensity of the colour is developed within 5-20 min and is stable for 2 hr.

Effect of pH : The optimum pH range for complete colour development is 2.0-3.1 with all aromatic amines. Above pH 7.0, the colour begins to fade slowly. All studies are confined to pH 3.0 ± 0.1.

Amount of catechol : 0.5-1.5 ml of 0.1% catechol solution is required for maximum colour development. 1 ml of 0.1% catechol was used.

Effect of oxidizing agent : A study was made of the use of various oxidizing solutions to be employed in the formation of the coloured species with catechol and aromatic amines. It was found that iron(III) (1 ml ; 0.02 *M*), sodium metaperiodate (1 ml ; 0.01 *M*), ammonium vanadate (2 ml ; 0.01*N*), chromium(VI) (1 ml ; 0.05 *N*), cerium(IV) (2 ml ; 0.01 *N*), hexacyanoferrate(III) (2 ml, 0.01*N*) or iodine (1 ml ; 0.01*N*) was necessary for complete colour development. If hydrogen peroxide is used, the experimental conditions are to be modified (catechol, 2 ml of 0.5% ; hydrogen peroxide, 1 ml of 1.8 *N* ; *p*H 2.1) and the time taken for complete colour development is 30-50 min. Of these oxidising agents, iodine was preferred as it gave maximum colour development within 5-20 min possessing considerable stability.

Effect of the order of addition : The order of addition of reagents does not have any influence on the colour development, if mixing is carried out immediately or adding catechol at the end even after 30 min. However, any delay in mixing aromatic amine to catechol-iodine reagent causes considerable decrease in absorbance.

Beer's law limits, molar absorptivity values and % recoveries are given in Table 1. The values obtained by the proposed method and the Bratton-Marshall method for dosage forms are given in Table 2. Ten replicate determinations were made with a typical aromatic amine (aniline) and the relative standard deviation was found to be 0.4%. The advantage of this new method is that it works with most of the dosage forms of aromatic amines and the results obtained are reproducible. Excipients and adjuncts usually present in dosage forms do not interfere. The other nitrogen bearing compounds such as aliphatic amines (primary, secondary and tertiary), cyclohexylamine, benzylamine, diphenylamine, 4-aminophenazone and N,N-dimethylaniline do not respond to the method.

TABLE 1—SPECTROPHOTOMETRIC ASSAY OF AROMATIC AMINES

Amine	Beer's Law limits μg/25 ml	Molar absorptivity at 520 nm $l\ mol^{-1}\ cm^{-1} \times 10^{-3}$	Recovery %
Aniline	25-150	1.1	99.4
o-Toluidine	50-250	2.9	99.8
p-Toluidine	50-300	[illegible]	99.1
p-Chloroaniline	50-300	1.4	98.4
p-Nitroaniline	50-250	1.1	97.9
Sulphanilic acid	50-200	4.[illegible]	99.7
p-Aminobenzoic acid	50-300	1.1	100.1
p-Phenetidine	50-300	1.6	99.3
Sulphanilamide	50-200	4.3	99.7
Sulphaacetamide	50-200	1.5	100.1
Sulphadimidine	50-200	1.5	99.8
Sulphamerazine	50-200	1.6	99.1
Sulphathiazole	50-200	4.9	99.3
Sulphamoxole	50-200	1.8	99.8
Sulphasomidine	50-200	1.7	99.4
Sulphamethizole	50-200	[illegible]	99.5
Sulphaphenazole	50-250	1.9	99.6
Sulphamethoxazole	50-150	1.6	100.2
Sulphapyridine	50-200	1.8	99.7
Benzocaine	50-200	5.0	99.9
Procaine	50-300	4.2	98.9
Dapsone	50-250	8.9	99.2
α-Naphthylamine	50-200	2.9	98.8
β-Naphthylamine	50-300	1.6	99.1
[illegible]-Methylaniline	25-100	1.2	99.5
Acetyl sulphathiazole*	50-150	2.9	100.3
Chloramphenicol**	50-200	3.1	100.5
Folic acid***	50-150	2.8	100.8

*After hydrolysis **After reduction *** After reduction and applying suitable correction for free amine and using *p*-aminobenzoic acid as standard

TABLE 2—ASSAY OF PHARMACEUTICAL AROMATIC AMINES IN DOSAGE FORMS

Dosage form	Nominal content g	Found, g	
		Proposed method	Bratton-Marshall method
Tablets			
Sulphadimidine, I P	0.500	0.493	0.495
Madribon-Sulphadimethoxine, B P	0.500	0.487	0.491
Lederkyn-Sulphamethoxy pyridazine, B P	0.500	0.502	0.508
Sulphapyridine, B P	0.500	0.485	0.493
Sulphuno-Sulphamoxole, B P	0.500	0.481	0.485
Elkosin-Sulphasomidine, B.P	0.500	0.494	0.498
Thiazole-Phthalyl sulphathiazole, I P	0.500	0.476	0.484
Folic acid, I P	0.050	0.048	0.047
Capsules			
Chloramphenicol, I P	0.250	0.244	0.246
Eye drops			
Albucid-sulphacetamide sodium, I P	1.420	1.38	1.40

Interferences The following amounts (ppm) of other constituents usually present in dosage forms are found to give less than 3% error in the determination of aromatic amines (e.g. sulphathiazole) talc (250), magnesium stearate (300), calcium phosphate (250), sodium chloride (350), chloramphenicol (250), penicillins (250), tetracycline (60), streptomycin (150), glucose (500) and trimethoprim (100).

Mechanism Titrimetric studies to know the reactivity of iodine separately with catechol and aromatic amine (sulphanilamide) at *p*H 3.1 revealed that iodine reacts almost completely within 15 min with catechol, whereas it does not react at all with sulphanilamide even after 1 hr. It is well known that oxidation of catechol under acidic conditions with oxidizing agents takes place in two steps, each involving removal of one electron, first to the semiquinone (purple-red colour) then to the *o*-benzoquinone[4,5]. If catechol-iodine reagent is replaced by *o*-benzoquinone in the general procedure, development of purple-red colour does not take place indicating that *o*-benzoquinone is not involved. Probably the intermediate semiquinone (because of resonance stabilisation, possesses longer life time and do not tend to attack the solvent or to initiate olefinic polymerisation) interacts with aromatic amine for the colour development. The composition of the coloured species formed between catechol (excess)-iodine reagent (semiquinone) and primary aromatic amine was determined spectrophotometrically using Job's continuous variation

and slope ratio methods. These methods show that iodine and primary arylamine combine in a 2 : 1 molar ratio. The failure in getting colour in alkaline pH clearly rules out the possibility of oxidative coupling between aromatic amine and catechol and so it is regarded as charge-transfer complex. The charge transfer may be presumed to be taking place involving electron transfer from the highest occupied π molecular orbital of the primary arylamine to the lowest unoccupied molecular orbital, π^*, of the semiquinone radicals as in the case of metol NBS reagent[6].

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Spectrophotometric Determination of Palladium with Rubeanic Acid in Presence of Piperidine, Quinoline, α-Picoline and Collidine

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RUBEANIC acid in conjunction with different organic heterocyclic bases have been utilised to estimate Pd, Co and Ni[1,4-7]. It has been found that piperidine, quinoline, α-picoline and collidine also enhance the colour and solubility of Pd(II) complex of rubeanic acid as a result of which rubeanic acid and one of the above four heterocyclic aromatic bases make a suitable ligand pair for the determination of palladium spectrophotometrically. Among the four bases studied, collidine is found to form the most effective ligand pair with rubeanic acid, the molar extinction coefficient in this case being distinctly higher than in other systems. The yellow colours which are developed in the above four systems have been found to absorb maximally at 380 nm in case of piperidine and quinoline and at 410 nm in case of α-picoline and collidine. The optimum pH range has been found to be 7-10.5 in each of the four systems where Beer's Law is obeyed.

Experimental

Chemicals, reagents and apparatus : Palladium solution was standardised by dimethylglyoxime. A 0.1% solution of rubeanic acid was prepared in 95% ethyl alcohol. The solution was found to remain stable for several days. 10% solution of each, in distilled ethanol, were obtained from freshly distilled piperidine, quinoline, α-picoline and collidine (analytical grade).

All absorbance measurements were made with a Hilger-Uvispek spectrophotometer. The pH values are determined with an Elico Model LI-10 pH meter, the later values being with respect to aqueous alcoholic solution.

Procedure To a slightly acidic solution of palladium, free from interfering ions, 1 ml reagent solution (0.1% w/v) was added after the addition of any of the four bases for determinations with piperidine, quinoline, α-picoline or collidine. 2 ml piperidine, 5 ml quinoline, 3 ml α-picoline and 2 ml collidine were added before the addition of the reagent. The final volume was made up to 25 ml with distilled alcohol and the absorbance measured at 380 nm for piperidine and quinoline and at 410 nm for α-picoline and collidine. The results of the above investigations are represented in Table 1.

Composition of the complexes The composition of the complexes as determined by Job's method of continued variation[8] and molar ratio method[8] shows that there are two different species with different heterocyclic base systems. While with pyridine and collidine, the presence of 1 : 1 metal : rubeanic acid ratio is observed, the 1 : 2 system seems to be predominant in other three systems (piperidine and rubeanic acid, quinoline and rubeanic acid and α-picoline and rubeanic acid). Bobtelsky and Eisenstadter[8] found by heterometric titration and micro analysis of the dried product that palladium combines with rubeanic acid to afford a number of compounds having the composition Pd_2Rba_3, PdRba, Pd_2Rba_3 and $PdRba_2$ (where Rba = rubeanic acid molecule or its radical) depending on the pH of the medium during precipitation and the amount of reagent present[8]. In the present case the units containing one Pd ion (1 : 1 and 1 : 2 variety) seems to be stabilised by the additional ligation of heterocyclic bases.

The results of Job's method and molar ratio method of the four systems are represented graphically (Figs. 1-8).

TABLE—1

Metal ion.	Reagents	Beer's Law and optimum range	Sensitivity	Molar extinction coefficient
Pd^{2+}	Rubeanic acid and piperidine	1-8.4 ppm 3-8.4 ppm	0 017 μg Pd/cm²	6246
Pd^{2+}	Rubeanic acid and quinoline	0.69-4.1 ppm 1.7-4.1	0.018 μg Pd/cm²	8129
Pd^{2+}	Rubeanic acid and α-picoline	0.625-4.875 ppm 1 87-4.8 ppm	0 019 μg Pd/cm²	5319
Pd^{2+}	Rubeanic acid and collidine	0.625-4.875 ppm 1.87-4.8 ppm	0 0104 μg Pd/cm²	10211
Pd^{2+}	Rubeanic acid and pyridine	1-10 ppm	0.0148 μg Pd/cm²	7224
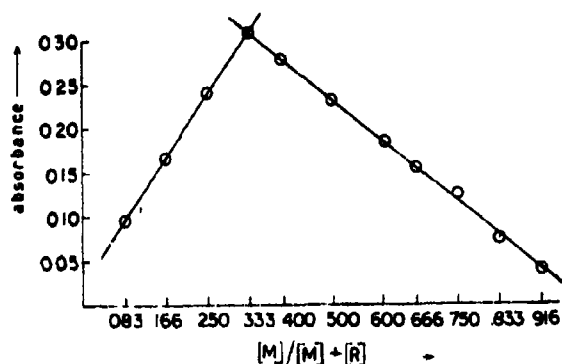
Fig 1 Job's method of composition Pd(II) Rubeanic acid piperidine complex
Pd(II) = Rubeanic acid = 5.588×10^{-4} *M*
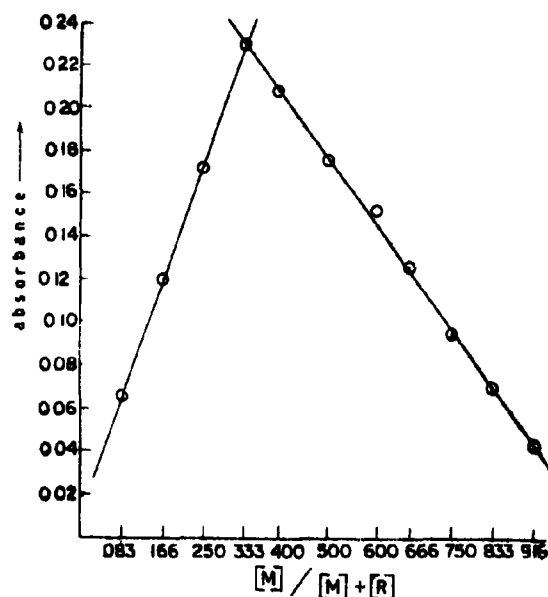
Fig. 3 Job's method of composition Pd(II) Rubeanic acid quinoline complex
Pd(II) = Rubeanic acid = 5.2875×10^{-4} *M*.
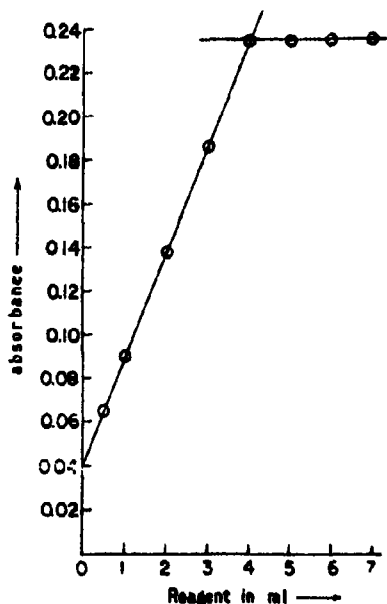
Fig 2. Molar ratio method of composition. Pd(II) Rubeanic acid piperidine complex.
Pd(II) = Reagent = 5.588×10^{-4} M.
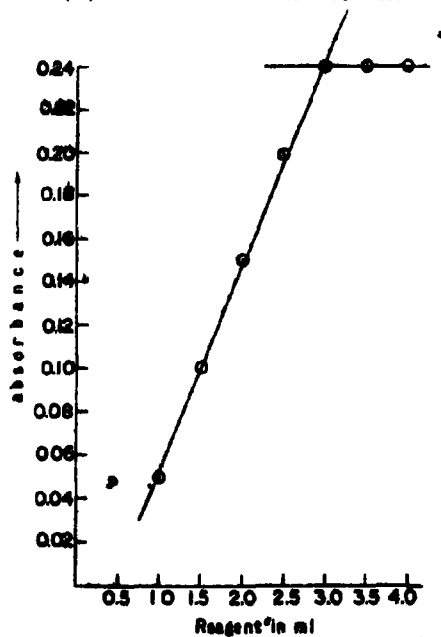
Fig. 4. Molar ratio method of composition. Pd(II) Rubeanic acid quinoline complex.
Pd(II) = Rubeanic acid = 5.588×10^{-4} *M*
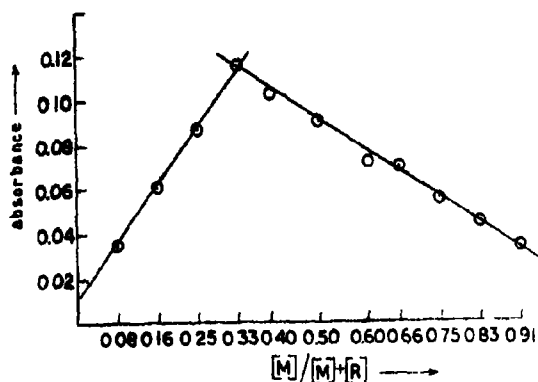
Fig. 5 Job's method of composition. Pd(II) Rubeanic acid α-picoline complex.

Pd(II) = Rubeanic acid = 1,175 × 10^{-4} M
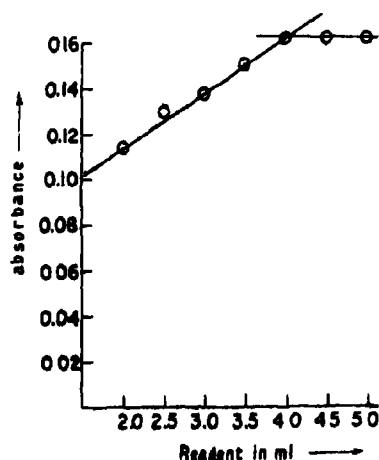
Fig 6 Molar ratio method of composition. Pd(II) Rubeanic acid α-picoline complex

Pd(II) = Rubeanic acid = 1 7625 × 10^{-4} M
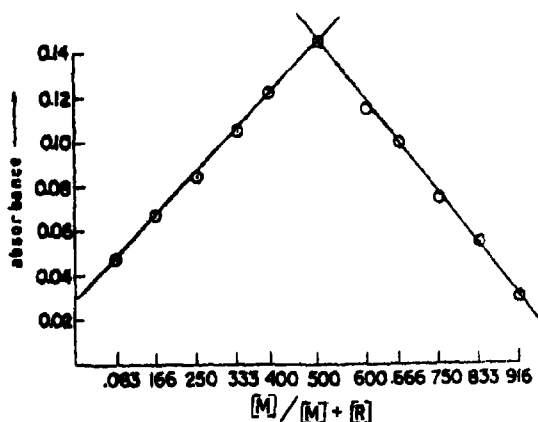
Fig. 7. Job's method of composition. Pd(II) Rubeanic acid collidine complex.

Pd(II) = Rubeanic acid = 1.175 × 10^{-4} M.
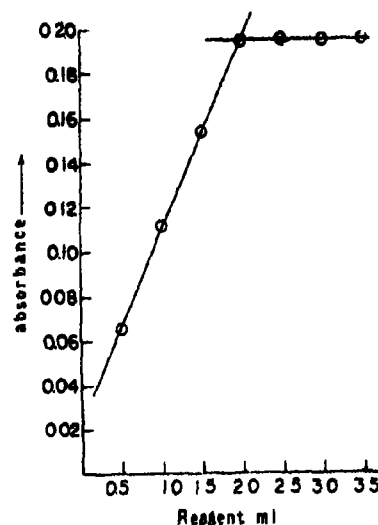
Fig 8 Molar ratio method of composition. Pd(II) Rubeanic acid collidine complex

Pd(II) = Rubeanic acid = 1.7625 × 10^{-4} M

Effect of diverse ions : Solutions were prepared in the same way as described under absorbance curve with 2.5 ppm of palladium(II) in each case containing different amounts of each ionic species whose effects were studied. It is observed that copper(II), cobalt(II), nickel(II), platinum(IV), molybdenum(VI), vanadium(V), tungsten(VI), manganese(II) and chromium(III) interfered with the determination

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Oxalyldihydrazide : A New Reagent for Rapid Gravimetric Determination of Selenium

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THE growing importance of selenium in industry and chemistry is reflected by the large number of papers dealing with its determination by

different methods which have been nicely reviewed[1,2]. The literature contains a number of methods based on the reduction of selenium(IV) and selenium(VI) to elemental selenium[3-14]. Based on the above principle the present paper describes the use of oxalyldihydrazide as a very convenient reagent for gravimetric determination of selenium. The method described allows rapid determination of selenium up to a minimum 5 mg. It has also been applied to selenium and tellurium mixtures for simultaneous estimation of both. Estimation of selenium can be done in the presence of several other foreign ions without the use of any masking agent

Experimental

Apparatus : The elemental selenium was collected on a sintered glass crucible (porosity G 4). A single pan semi-micro balance, VEB Analytik SAHM-68, was used for weighing

Reagents :

(a) *Selenium solution* : The selenium solution was prepared by dissolving reagent grade sodium selenite and the amount of selenium was gravimetrically determined by both sulphur dioxide[15] and hydroxylamine[15] methods. A working solution of 2 mg/ml Se was prepared by dilution

(b) *Oxalyldihydrazide solution* A 2% w/v solution of oxalyldihydrazide was prepared in water The reagent was prepared by reported method[16].

(c) Solution of foreign ions were prepared by the method of West[17]

AnalaR grade HCl was used to maintain the acidity.

Procedure A suitable aliquot of standard selenium solution was transferred to a beaker and diluted. 10 ml of 2% oxalyldihydrazide solution was added and the acidity maintained between 2-3 *M* with HCl to a final volume of 100 ml. The solution was boiled for 15 min for complete reduction and was filtered while warm on a sintered glass crucible. The precipitated selenium was washed with water and alcohol, dried at 110° and weighed. Results are shown in Table 1.

TABLE 1—RECOVERY OF SELENIUM

Acidity = 3 M HCl

Sl. No	Se taken mg	Se obtained* mg	Error %	Recovery %
1	10	10.01	+0 10	100 10
2	40	40 02	+0.05	100.05
3	100	99.98	-0 02	99.98
4	150	150.02	+0.01	100 01
5	250	250.09	+0 04	100 04

*Mean of five replicates.

Determination of selenium and tellurium : Synthetic samples containing definite amounts of selenium and tellurium were prepared. Selenium was determined by the recommended procedure. For the determination of tellurium, the filtrate was concentrated, 20 ml of 2% oxalyldihydrazide was added and the acidity was fixed to 6 *M* and above. The solution was boiled for 1 hr for complete reduction of tellurium. The precipitated tellurium was filtered on a sintered glass crucible, washed with water and alcohol, dried at 110° and weighed. Results are shown in Table 2.

TABLE 2—SELENIUM-TELLURIUM ANALYSIS IN SYNTHETIC SAMPLES

Acidity for Se = 3 *M* HCl
Acidity for Te = 6 *M* HCl

Se taken mg	Te taken mg	Se found* mg	Te found* mg	Se Recovery %	Te Recovery %
20	10	19 97	10 02	99.80	100 20
20	20	19 98	19 99	99.90	99.95
20	40	20 01	40 01	100 05	100 02
40	60	39 99	60 01	99 97	100.01
40	100	39.98	99 98	99 95	99 98

*Mean of three replicates

Results and Discussion

Preliminary experiments were conducted to find out the optimal conditions for complete reduction. The influence of the variables have been investigated.

Acidity : The optimal acidity range for complete reduction of selenium was found to be 2 5 to 8 *M* HCl. Effect of other acid media for reduction process was also studied. The reduction took more time in case of sulphuric acid and acetic acid whereas no reduction took place in case of nitric acid.

Amount of reagent : It was found out that 10 ml of 2% solution of oxalyldihydrazide was sufficient for the reduction of 250 mg of selenium.

Effect of foreign ions : Studies revealed that up to 20 fold excess of the following ions do not interfere : Cu(II), Ni(II), Mg(II), Mn(II), Zn(II), Hg(II), Cd(II), Co(II), Bi(III), Al(III), Sb(III), Fe(II), Fe(III), Sr(II), V(V), Nb(VI), Mo(VI), Ti(IV), Th(IV), Be(II), and up to 50 fold excess of NO_3^-, PO_4^{3-}, tartrate, citrate, EDTA, SO_4^{2-}. In case of Ce(III), Cr(VI) and Fe(III), larger amount of reagent and longer heating time were required. Only tungsten interferes in the system but it can be first precipitated and then selenium can be determined in the filtrate.

Comparison with other methods : The proposed reagent is very suitable and selective for the determination of selenium. The reagent can be easily prepared, is stable and can be stored for long periods which is not possible with many of the reported methods[8,11,12,14]. Another outstanding feature of this reagent is that it can be used for simultaneous estimation of selenium and tellurium.

The method is very fast as compared to other methods[16].

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Detection and Determination of Phosphate Using Monomethyl-*p*-Amidophenol as Reagent

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MOST of the methods available for the detection and determination of phosphate are indirect involving complexation of phosphate with molybdenum(VI) and subsequent reduction of the phosphomolybdate. The reagents used for the detection of phosphate are ammonium molybdate and benzidine[1], *o*-dianisidine molybdate and hydrazine[2], quinolinium molybdate[3] and ammonium molybdate and triphenyl methane dyes[4,5]. The reducing agents used for the development of the blue colour are tin(II) chloride[6], hydroquinone[7], hydrazine sulphate[8], ascorbic acid[9] and 1,2,4-aminonaphthol sulphonic acid[10]. A few other methods, involving extraction of the blue colour into an immiscible organic layer are also reported. Very few reports are available for direct detection and determination of phosphate.

The method for detection and determination of phosphate reported in this communication, is a simple and direct one. The phosphate in solution, on reaction with monomethyl-*p*-amidophenol in 1-5 *N* HCl or in 1-10 *N* H_2SO_4, will oxidise it to purple-red *p*-N-methylquinone. The absorption spectrum of the purple-red coloured solution gives maximum absorption at 525 nm.

Materials and method :

Standard phosphate solution : 0.2197 g of potassium dihydrogen phosphate (previously dried at 110° for 1 hr and cooled in a desiccator) is dissolved in deionised water and diluted to 1 litre in a volumetric flask. 1 ml of this solution contains 0.05 mg P.

Monomethyl-p-amidophenol solution : 0.05 *M* solution is prepared by dissolving 17.190 g of the reagent (AnalaR grade) in 1 litre deionised water and standardised vanadometrically[11].

All other reagents used are of AnalaR grade unless otherwise mentioned.

Beckmann-26 spectrophotometer with auto recorder is used for spectral measurements.

Experimental

Detection of phosphate in a test tube : 0.5 ml of the test solution is taken in a test tube and 0.5 ml of monomethyl-*p*-amidophenol reagent solution is added followed by 1.5 ml of 2.5 *N* HCl. A purple-red colour develops immediately on shaking the test tube which indicates the presence of phosphate.

Limit of detection—2.63 μg/2.5 ml

Limit of dilution—1 : 2,000

Detection of phosphate on a spot plate : 0.04 ml of the test solution is taken in the cavity of the spot plate. 0.04 ml of the reagent followed by 0.04 ml HCl (1 : 4) are added and mixed with a glass rod. An immediate purple-red colour, stable for 48 hr indicates the presence of orthophosphate.

Limit of detection—0.53 μg/0.12 ml

Limit of dilution—1 10,000

Photometric determination of phosphate : To a known volume of the sample solution containing 4-13 μg of P in a 10 ml volumetric flask are added successively 3 ml of 0.05 *M* monomethyl-*p*-amidophenol and 1 ml of conc. HCl. The volume is made up to the mark with distilled water. The absorbance of the purple-red coloured solution, the oxidation product of the reagent, is measured at 525 nm against a reagent blank.

Typical results are presented in Table 1.

Results and Discussion

By preliminary experiments it is found that the acidity should be in between 1-5 *N* for HCl and

TABLE 1—SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHATE USING MONOMETHYL-p-AMIDOPHENOL AS REAGENT

Sl. No.	Sample	Taken	P in μg found*	Standard deviation
1.	Na_3PO_4	4.9274	4.9280	±0.01591
2.	Na_2HPO_4	8.2125	8.2128	±0.01190
3.	Na_2HPO_4	9.0652	9.0695	±0.01807
4.	$(Ca)_3(PO_4)_2$	11.8879	11.8888	±0.02901
5.	NPK fertiliser	10.6488	10.6486	±0.02273
6.	NPK fertiliser	6.5261	6.5264	±0.00702

* Average of five readings.

1-10 N for H_2SO_4. Below 1 N the colour development is rather slow and above 5N (10 N for H_2SO_4) the colour developed gets discharged. HCl medium is preferred to H_2SO_4 as the colour developed in H_2SO_4 medium is less stable due to the heat developed in the mixing process. The oxidation of the reagent to p-N-methylquinone takes place readily in acid medium. It is observed that the colour attains maximum intensity within 5min after mixing the reagent and remains stable for 48 hr, if the reductant is in excess.

The reagent prepared in distilled water is stable for 4 hr. The stability can be enhanced up to 10 hr if preserved in ambered coloured bottles. On prolonged preservation a brownish-red colour develops in the reagent solution due to aerial oxidation and this interferes in the process of oxidation by phosphate.

It is found that chloride, bromide, sulphate, metaborate, thiocyanate, silver(I), gelatin, p-hydroxyglycine, acetone, hydroquinone, iron(II), tin(II), arsenic(III), triphosphates or tetraphosphates do not interfere in the said conditions, but dichromate, cerate, quinones, citrate, oxalate, sulphite and bisulphite interfere seriously.
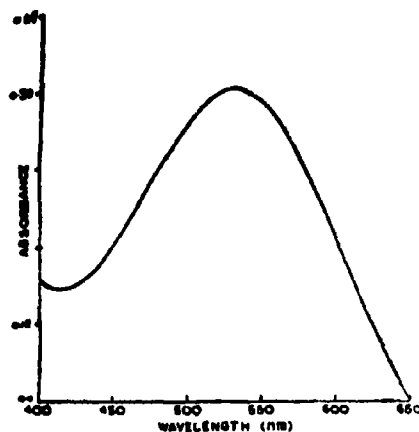
Fig 1 Absorbance spectrum of oxidation product of monomethyl-p-amidophenol with phosphate

Acknowledgement

The authors are thankful to the C.S.I.R., New Delhi, for the award of Junior Research Fellowship to one of them (A.V.S N.).

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Book Review

Experimental Organic Chemistry by P. R. Singh, D. S. Gupta and K. S. Bajpai, Tata McGraw-Hill, 1981, Vol. 1. xvii+267 (Rs. 27.00) ; Vol. 2 xix+378 (Rs. 27.00).

This book is designed as a text for an advanced undergraduate as well as post-graduate course in practical organic chemistry. Keeping in view its objectives, the development of theoretical background for experimental work, depth of coverage, selection of the list of experiments and the price make it an ideal choice both for the students as well as for the teachers. The book has been written in a lucid, non intimidating manner without, however, sacrificing the finer experimental details, wherever necessary.

The first volume deals with the preparative aspect of the practical organic chemistry. This has been divided into two parts comprising thirteen chapters. The first part concerns the basic techniques of practical organic chemistry presenting the subject matter in reasonable detail with inclusion of a brief introductory chapter on the working in the laboratory and safety measures.

A full chapter has been devoted to the Chromatographic Techniques which are now imperative in experimental organic chemistry. The chapter is well illustrated and all the necessary details are briefly incorporated.

The chapter on Spectroscopic Techniques, though enhances the utility of the book, is conspicuously inadequate. Although it includes the necessary theoretical and experimental details of IR, UV, PMR and Mass spectroscopic techniques, it lacks some illustrative problems of simple structural elucidation based on the combined use of these methods. Nevertheless, the Tables are quite comprehensive which, to some extent, covers this lapse.

The chapter seven, "Sources of Library Information" provides a list of useful current reference books, journals and abstracts.

The second part of volume one covers organic preparations which have been logically classified into several groups based on reaction mechanism. Each chapter first provides a brief introduction to the relevant reaction mechanism followed by experimental details of some selected preparations. Although the preparations are reasonably diversified, it appears that some pages could have been saved here and added more beneficially to the chapter on Spectroscopy, as mentioned above.

Volume Two has also been divided into two parts. The first part dealing with Qualitative Analysis comprises seven chapters. This part has been written in a routine manner. The characteristic IR absorption peaks have also been given for each class of compounds. However, it would have been better, had the IR spectrum of a representative compound of each class been reproduced. The Tables include a sufficient number of organic compounds with their relevant properties.

Part two concerns Quantitative Analysis including estimation of elements and functional groups followed by some experiments on Reaction Kinetics and some Miscellaneous Experiments. All the relevant details have been described briefly and this part seems complete in itself. Some experiments of industrial importance have also been incorporated in this section.

Each chapter ends with a few problems, which in some cases form a corollary to what has been described in that particular chapter. Many problems are quite interesting and are likely to induce the students to develop insight in the subject.

The appendices contain hints to some selected problems given in the chapters, as well as additional bibliography, methods of preparation of reagents and indicators and also some physical constants.

In summary, it can be said that this book succeeds in its objective of providing all the material of practical organic chemistry at one place to those for whom this book has been written.

R. K. Bansal

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Vol. LIX, October 1982, pp. 1117-1120

Metal Complexes of Some Model Peptides. Part—I : Complex Formation of Cu(II) with N-Salicyloyl Glycine

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*p*H-Metric study of the interaction of Cu(II) with N-salicyloyl glycine, *o*-(OH)-$C_6H_4CONHCH_2COOH$, LH_3, indicated the stepwise formation of 1 : 1 and 1 : 2 metal : ligand complexes. The phenolic –OH group was not involved in coordination to Cu(II), as its deprotonation occurred only after the completion of formation of the 1 : 2 complex. Coordination from the N-(peptide) atom occurred only through deprotonation. The stepwise equilibrium constants (K'_1 and K'_2) of complex formation, stepwise deprotonation constants (k_{2OH} and k_{1OH}) of the 1 : 2 complex, $Cu(LH)_2^{2-}$ ion and successive acid dissociation constants (k_{COOH}, k_{OH} and k_{NH}) of the ligand LH_3 have been determined. The overall stability constants, β_{pqr} of the complexes $[Cu_pH_qL_r^{+2p+q-3r}]$ have been calculated. The pK'_1, pK'_2, pk_{2OH}, pk_{1OH}, pk_{COOH}, pk_{OH}, pk_{NH}, $\log \beta_{111}$, $\log \beta_{122}$, $\log \beta_{112}$ and $\log \beta_{102}$ values have been found to be 6.54±0.04, 6.76±0.04, 8.68±0.04, 9.46±0.04, 4.26±0.02, 9.12±0.04, 12.88±0.04, 6.84±0.04, 13.46±0.04, 17.66±0.04 and 21.08±0.04, respectively at 30±0.5° in 50% (v/v) water-ethanol at a constant ionic strength μ=0.2 *M* ($NaClO_4$). Trends in the pk_{OH} values of the free and of the complexed ligand and the equilibrium distribution of the complex species have been discussed.

THE model peptide ligand N-salicyloyl glycine, *o*-(OH)$C_6H_4CONHCH_2COOH$, (LH_3) is widely used as an antiinflammatory drug[1]. In the present work its interaction with Cu(II) ion has been followed *p*H-metrically at 30±0.5° in 50% (v/v) water-ethanol medium at a constant ionic strength, μ= 0.2 *M* ($NaClO_4$). The study indicated the stepwise formation of 1 : 1 and 1 : 2 metal : ligand complexes in which coordination to the metal was provided by the carboxylic oxygen and the N-(peptide) atom of the ligand. Coordination of the N-(peptide) atom occurred only on deprotonation[2-13]. Deprotonation of the phenolic-(OH) group occurred only after the completion of the formation of the 1 : 2 complex suggesting non-involvement of this group in coordination.

Experimental

The ligand, N-salicyloyl glycine, was prepared and purified by the reported procedure[14]. All other reagents were either of A. R. quality or properly purified and their solutions were made in double distilled CO_2 free water and purified and dry ethanol[15].

*p*H-Metric titrations of 50 ml solutions of the following compositions :

(i) 0.02 *M* $HClO_4$,

(ii) 0.02 *M* $HClO_4$+0.01 *M* LH_3,

(iii) 0.02 *M* $HClO_4$+0.01 *M* LH_3+0.001 *M* $Cu(ClO_4)_2$

(iv) 0.02 *M* $HClO_4$+0.01 *M* LH_3+0.002 *M* $Cu(ClO_4)_2$

were performed in 50% (v/v) water ethanol medium with a standard NaOH solution in the same solvent medium maintaining a constant ionic strength, μ=0.2 *M* by adding requisite amounts of $NaClO_4$, at 30±0.5°. *p*H measurements were made with a Cambridge *p*H-meter (Portable type) having a glass electrode of 1-13 *p*H range and a saturated calomel electrode connected to the cell by means of an agar 2 *M* $NaNO_3$ bridge. The meter was calibrated using standard 0.02 *M* $HClO_4$, phthalate buffer and borate buffer solutions with appropriate temperature corrections.

Titrations curves, *p*H vs volume of alkali, were drawn (Fig 1) and the necessary concentration variables e g. $\bar{n}_H$, $\bar{n}$, n_{OH}, pLH_2 etc. were calculated following the procedure of Irving and Rossotti[16].

Results and Discussion

Stepwise acid dissociation of N-salicyloyl glycine (LH_3) :

Consumption of more than two equivalents of alkali per mole of the ligand N-salicyloyl glycine in the *p*H range 2.5 to 12.5 in the titration of solution (ii) indicated three successive steps of its acid dissociation as represented by the equilibria (1)-(3).

$$o\text{-(HO)}C_6H_4CONHCH_2COOH \overset{k_{COOH}}{\rightleftharpoons} o\text{-(HO)}C_6H_4CONHCH_2COO^- + H^+ \quad \ldots (1)$$

$$o\text{-(HO)}C_6H_4CONHCH_2COO^- \overset{k_{OH}}{\rightleftharpoons} o\text{-(O)}C_6H_4CONHCH_2COO^{2-} + H^+ \quad \ldots (2)$$

$$o\text{-(O)}C_6H_4CONHCH_2COO^{2-} \underset{}{\overset{k_{NH}}{\rightleftharpoons}} o\text{-(O)}C_6H_4CONCH_2COO^{3-} + H^+ \quad (3)$$

where k_{COOH}, k_{OH} and k_{NH} are the successive acid dissociation constants. The possibility of enolisation, $-CONH- \rightleftharpoons -C(OH)=N-$, of the peptide

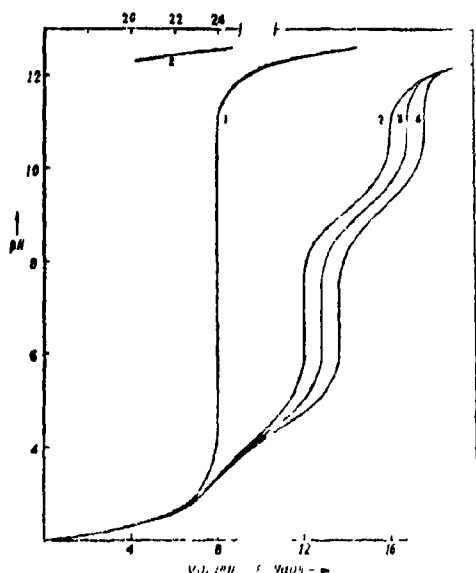



Fig. 1. pH-titration curves. Initial volume 50 ml in 50% (v/v) water-ethanol, ionic strength, $\mu = 0.2$ ($NaClO_4$) in each case.

Curve 1 : 0.02 *M* $HClO_4$.

Curve 2 : 0.02 *M* $HClO_4$ + 0.01 *M* N-salicyloylglycine. (LH_2).

Curve 3 : 0.02 *M* $HClO_4$ + 0.01 *M* N-salicyloylglycine, (LH_2) + 0.001 *M* $Cu(ClO_4)_2$.

Curve 4 : 0.02 *M* $HClO_4$ + 0.01 *M* N-salicyloylglycine. (LH_2) + 0.002 *M* $Cu(ClO_4)_2$.
Titrant : 0.125 *M* NaOH ($\mu = 0.2$)

group could not, however, be ruled out. The plot of $\bar{n}_H$ (the average number of protons bound to the ligand ion, L^{3-}) against *p*H showed that the steps (1), (2) and (3) were all independent of one another and therefore, the constants k_{COOH}, k_{OH} and k_{NH} were evaluated by curve fitting method for one step system and also by the method of linear plots. The refined pk_{COOH}, pk_{OH} and pk_{NH} values are given in Table 1.

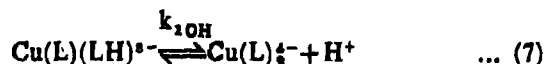
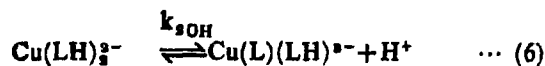
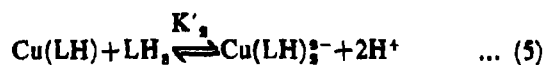
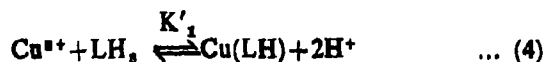
Complexation of Cu(II) with N-salicyloyl glycine :

The nature of the *p*H titration curves of the ligand solution in the presence of Cu(II) (curves 3, 4 ; Fig. 1) indicated the liberation of four equivalents of acid per gm ion of the metal in the *p*H range from 2.5 to 7.0 and two further equivalents of acid in the *p*H range from 7.75 to 10.50. The buffer region corresponding to the liberation of the latter two equivalents of acid was practically the same as that was corresponding to the deprotonation of the $-OH$ group of the ligand in the absence of Cu(II). Therefore, the liberation of four equivalents of acid at the early stages of the reaction below *p*H 7 is clearly due to coordination of $-COOH$ group and N-(peptide)[17] atom to Cu(II) each with deprotonation, ultimately leading to the formation of the 1 : 2 complex $[Cu(LH)_2]^{2-}$, according to the reactions (4) and (5), and these were followed by the deprotonation of the phenolic-OH groups not coordinated to the metal in the *p*H range 7.75-10.50 in a stepwise manner according to the reaction (6) and (7) :

$$Cu^{2+} + LH_3 \overset{K'_1}{\rightleftharpoons} Cu(LH) + 2H^+ \quad \dots (4)$$

$$Cu(LH) + LH_3 \overset{K'_2}{\rightleftharpoons} Cu(LH)_2^{2-} + 2H^+ \quad \dots (5)$$

$$Cu(LH)_2^{2-} \overset{k_{2OH}}{\rightleftharpoons} Cu(L)(LH)^{3-} + H^+ \quad \dots (6)$$

$$Cu(L)(LH)^{3-} \overset{k_{1OH}}{\rightleftharpoons} Cu(L)_2^{4-} + H^+ \quad \dots (7)$$

where K'_1, K'_2, k_{2OH} and k_{1OH} are the equilibrium constants of the respective complexation and deprotonation steps and LH^{2-} stands for the ligand ion $o\text{-(HO)}C_6H_4CONCH_2COO^{2-}$.

The presence of the phenolic-OH group in the isolated compound $Cu(LH).2H_2O$ was indicated by the appearance of an itense violet colour on addition of neutral $FeCl_3$ to its aqueous ethanolic solution and also by the appearance of a broad ir band in the region 3500-3000 cm^{-1}. The green compound $Cu(LH).2H_2O$ was obtained by treating a solution of the ligand LH_3 (0.1 mole) with equimolar amount of copper sulphate solution in hot water and adjusting the *p*H to$\approx$4.5 It was recrystallised from ethanol, air dried and analysed. Found : Cu, 21.86 ; N, 4.29 ; loss at 105°, 12.17%. Calcd. for $Cu(LH).2H_2O$; Cu, 21.72 ; N, 4.78 ; H_2O, 12.31%. Metal : ligand ratios in the complexes formed in solution were also determined spectrophotometrically at 610 nm by the method of continuous variation, under the same experimental conditions at two different *p*H values, viz., at *p*H = 7 where $\bar{n} \approx 4$ and at *p*H$\approx$11 where $\bar{n}_{OH} \approx 0$ At both the *p*H values the maximum absorption corresponded to the 1 : 2 metal : ligand ratio. Therefore, liberation of acid at *p*H values higher than 7 was due to deprotonation of the 1 : 2 complex, and not due to the formation of higher complexes. The pK'_1 and pK'_2 values were evaluated from the plot of $\bar{n}$, the average number of protons liberated due to reactions (4) and (5), against $pLH_3 - 2pH$ and were refined by various computational methods[17]. The $\bar{n}$ values were calculated using portion of the titration curves (3 and 4 ; Fig. 1) from *p*H 2.5 to *p*H 7.0 and assuming all the Cu(II) ions in the forms of Cu^{2+}, Cu(LH) and Cu $(LH)_2^{2-}$ ion, in this *p*H range. The values of pk_{2OH} and pk_{1OH} were evaluated from the plot of $\bar{n}_{OH}$, the average number of protons bound to the complex $[Cu(LH)_2^{2-}]$ ion against *p*H, assuming all the Cu(II) ions in the forms of the complexes $Cu(LH)_2^{2-}$, $Cu(L)(LH)^{3-}$

TABLE 1—PROTON LIGAND AND Cu(II)-LIGAND STABILITY CONSTANTS AT 30±0.5°, μ=0.2 (NaClO$_4$) 50% (v/v) WATER-ETHANOL

pk_{COOH}=4.26±0.02	pK'_1 =6.54±0.04,	log β_{111}=6.84±0.04
	pK'_2 =6.76±0.01,	log β_{122}=13.46±0.04
pk_{OH}=9.12±0.04	pk_{2OH}=8.68±0.04,	log β_{112}=17.66±0.04
pk_{NH}=12.88±0.04	pk_{1OH}=9.46±0.04,	log β_{102}=21.08±0.04

and $Cu(L)_2^{4-}$ in the pH range from 7.75 to 10.5, and were refined as before[1,7].

The overall stability constants[1,8,10] of these Cu(II) complexes of the general formula $[Cu_pH_qL_r^{(2p+q-rx)+}]$ as defined by the relation .

$$\beta_{pqr}=\frac{[Cu_pH_qL_r^{(2p+q-rx)+}]}{[Cu^{2+}]^p[H^+]^q[L^{x-}]^r} \quad \dots (8)$$

were calculated using p=1 and x=3. Concordance of duplicate titrations [soln (iii) and (iv)] using two different concentrations of the metal ion ruled out the possibility of formation of any polynuclear complex under the condition studied. The overall stability constants β_{111}, β_{122}, β_{112} and β_{102} have been evaluated from the relations :

$$\beta_{111}=\frac{[Cu(LH)^0]}{[Cu^{2+}][(LH)^{2-}]}=\frac{K'_1}{k_{COOH}k_{OH}} \quad \dots (9)$$

$$\beta_{122}=\frac{[Cu(LH)_2^{2-}]}{[Cu^{2+}][(LH)^{2-}]^2}=\frac{K'_1K'_2}{(k_{COOH}k_{OH})^2} \quad \dots (10)$$

$$\beta_{112}=\frac{[Cu(LH)(L)^{3-}]}{[Cu^{2+}][LH^{2-}][L^{3-}]}=\frac{\beta_{122}.k_{2OH}}{k_{NH}} \quad (11)$$

$$\beta_{102}=\frac{[Cu(L)_2^{4-}]}{[Cu^{2+}][L^{3-}]^2}=\frac{\beta_{112}.k_{1OH}}{k_{NH}} \quad (12)$$

The refined log β_{pqr} values are shown in Table 1.

Although the possibility of enolisation of the peptide group prior to deprotonation cannot be ruled out, metal ions such as Cu(II), Ni(II), Co(II) will prefer to bind with the N-(peptide) atom rather than the O-(peptide) atom because of the comparatively strong ligand field that the former can provide. In the absence of X-ray data, it is however, not possible to decide which atom of the peptide group is actually bonded to the metal in the complexes. The pk_{2OH} value of the complex $Cu(LH)_2^{2-}$ ion has been found to be slightly lower than the pk_{OH} of the ligand, LH_3, as a consequence of N-(peptide)→metal sigma bond formation. Due to much accumulation of negative charge on the metal, the subsequent deprotonation is, however, less favoured, even the possibility of some back donation through the pi-system of the peptide bond cannot be ruled out. As a matter of fact, pk_{1OH} of the complex is slightly higher than the pk_{OH} of the ligand. Equilibrium concentrations of the various species involved in the complexation reaction were calculated and the distribution curves (Fig. 2) were constructed. At pH near 7.0 almost

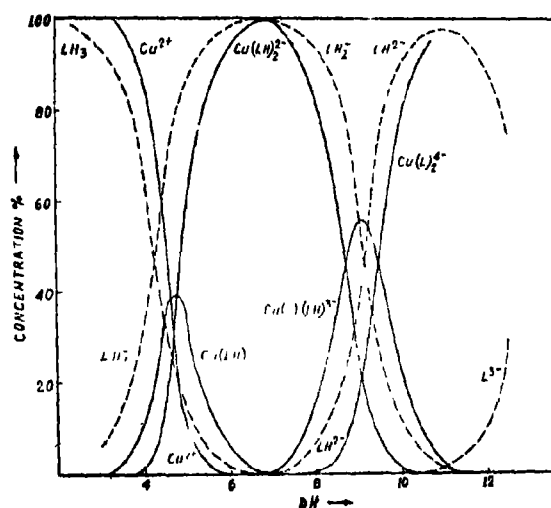



Fig. 2. Complex distribution curve.

all the metal remain in the form of the 1 : 2 complex $Cu(LH)_2^{2-}$ and concentration of the 1 : 1 complex Cu(LH) is negligible. Therefore, the assumptions made in the evaluation of the constant k_{2OH} and k_{1OH}, that the complexation steps (4) and (5) were not overlapping with the deprotonation steps (6) and (7) are justified.

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Stacked Ternary Complexes of Salicylanilide, Dithionon and Tryptophan with Co(II), Ni(II) and Cu(II)

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Formation constants of ternary complexes of the types MAL^+ and MAL [where M=Co(II), Ni(II) or Cu(II), A=dth(MAL^+) or trp(MAL) and L=trp(MAL^+) or sal(MAL)] have been determined in solution potentiometrically, to provide further evidence on complexation as a possible mode of action of fungicides. The formation tendency ($\Delta \log K_M$) of these complexes has been found to be positive for MAL^+ type of complexes which has been explained as being due to M→dth π-interaction and has also indicated intramolecular aromatic ring stacking between the ring systems of the two ligands. The negative values of $\Delta \log K_M$ have been found to be due to weak M→trp π-interaction and absence of intramolecular aromatic ring stacking.

It was observed in our previous investigation[1] that salicylanilide forms considerably stable complexes with some metal ions of biological interest, such as Co(II), Ni(II), Cu(II), Zn(II), Zr(IV), La(III) and Th(IV), thereby supporting complexation as a possible mode of action of this fungicide. Since some specific structural requirements[2] are essential for the occurrence of complexation and also for a compound to show activity[3], ternary complexes of salicylanilide (sal), dithionon (dth) and tryptophan (trp) with Co(II), Ni(II) and Cu(II) have been studied in solution to provide further evidence of complexation mechanism.

Experimental

Materials : The metal nitrates used were of A. R. grade. Salicylanilide was obtained from Boots Chemical, UK. Other chemicals were B.D.H. AnalaR grade. Dioxane was used after purification. A 70% aqueous dioxane (v/v) was chosen to keep salicylanilide, dithionon and their complexes in solution. All measurements were performed at constant ionic strength (0.1 M KNO_3) and constant temperature (25°).

Method : The binary systems were investigated with 1 : 2 molar ratio of metal ion and ligand while the ternary systems were studied in 1 : 1 : 1 molar ratio of a metal ion, a primary ligand (trp or dth) and a secondary ligand (sal or trp) in acidic and non-acidic medium. The change in the pH of the solution, with each addition of 0.1 M NaOH solution was recorded with a Beckman pH meter equipped with a glass-calomel assembly. The pH values were corrected for 70% aqueous dioxane (v/v) medium using the method of Van Uitert and Haas[4].

Calculations : The protonation constants and the stability constants (Table 1) of the parent binary complexes of sal and trp were calculated by computational methods of Irving and Rossotti[5]. Although most of the protonation and stability constants of parent binary complexes of trp are studied in aqueous medium[6,7], these were redetermined due to the change in medium of investigation. The stability constants of binary complexes of dth could not be calculated because evaluation of its protonation constant proved unsuccessful due to overlapping nature of the titration curves of ligand with or without mineral acid (HNO_3). It is

Table 1—Stability Constants of Binary and Ternary Metal Complexes of Salicylanilide, Tryptophan and Dithionon in 70% Aqueous Dioxane (v/v), μ=0.1 M (KNO_3), T=25°.

Primary ligand	Secondary ligand	Metal Ion	$\log K^M_{MA}$	$\log K^{MA}_{MA_2}$	$\log K^M_{ML}$	$\log K^{ML}_{ML_2}$	$\log K^M_{MAL}$	$\Delta \log K$
Trp	Sal	Co(II)	4.42	4.16	7.58	7.11	3.78	−0.80
		Ni(II)	5.51	5.10	7.72	7.35	6.82	−0.90
		Cu(II)	8.03	6.63	8.16	7.50	7.63	−0.53
Dth	Trp	Co(II)	–	–	4.42	4.15	4.77	+0.35
		Ni(II)	–	–	5.51	5.10	5.91	+0.40
		Cu(II)	–	–	8.08	6.63	8.71	+0.68

*Author for correspondence.

not essential to know the stability constants of these complexes while calculating the stability constants of their ternary complexes as it was observed in the case of 2,2'-bipyridyl complexes[8].

The stability constants of MAL^+ type of complexes were calculated using the method of L' Heureux and Martell[9] assuming dth as a primary ligand and trp as a secondary ligand because the nature of titration curve indicated the formation of 1 : 1, M-dth complex at very low *p*H which did not hydrolyse even at higher *p*H ~7. Some representative titration curves showing the sequence of addition of ligands and hydrolytic phenomenon are shown in Fig. 1. In MAL type of complexes trp has been considered as a primary ligand
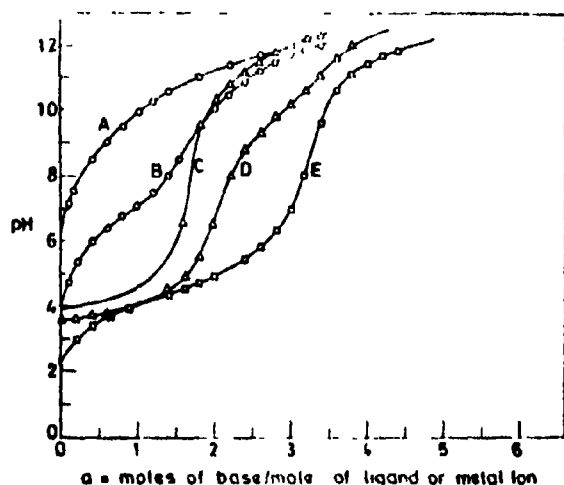
Fig 1. Representative potentiometric titration curves.
A : dth, B 1 : 1 ; Cu(II)-dth, C : trp,
D : 1 : 1 , Cu(II)-trp, E : 1 : 1 : 1, Cu(II)-dth-trp.
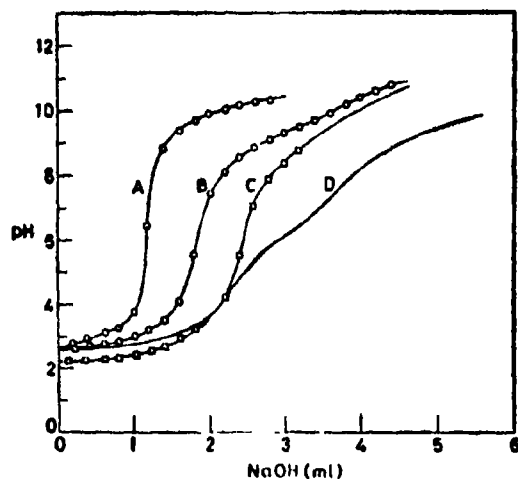
Fig. 2. Representative potentiometric titration curves.
A : HNO_3, B : HNO_3 + trp.
C . 1 : 1 , Cu(II)-trp, D : 1 : 1 : 1, Cu(II)-trp-sal.

because 1 : 1 M-trp complex hydrolyses at higher *p*H value than 1 : 1 M-sal complex. Further, the titration curve (Fig. 2) of 1 : 1 : 1 M-trp-sal runs slightly above the 1 : 1 M-trp curve, then superimposes and subsequently moves below it, thereby indicating the formation of 1 : 1 : 1 MAL complex after the complete formation of 1 : 1 M-trp complex. Hence, $K_{prim(trp)}$ $K_{sec(sal)}$ is not an essential requirement in the formation of ternary complexes. Such observations have also been noticed by Gergely *et al*[9] on the ternary complexes of α-amino acids The stability constants of MAL complexes have been calculated using modified form of Irving-Rossotti method[5] as employed by other workers[10]. These values have been listed in Table 1.

Results and Discussion

Binary systems : The protonation and the stability constant values are more sensitive to the dielectric constant of the medium than to ionic strength or temperature. In dioxane-water mixtures of low dielectric constant, these values were expected to be significantly higher than those for the aqueous medium. But in the present investigation these values are not according to known general trend. It is evident from Table 1 that in the case of M-trp complexes the stability constant data in dioxane-water mixture are lower than those in water. Such irregularities have also been reported in literature[6,7] on binary complexes of ligands containing N or N and O as donor atoms where the stability constants were generally found to be lower in solvents of low dielectric constants.

Ternary systems · All ternary systems revealed the formation of MAL^+ or MAL type of complexes only. Δ log K_M values (Table 1) are positive for MAL^+ but negative for MAL complexes. The positive values of Δ log K_M were found to be due to the discriminating properties of dth towards trp because in addition to N→M σ-bonding in dth complexes there also exist $M_{(d)} \rightarrow N_{(p)}$ π-bonding. This renders the charge and electronegativity of the metal ion in M-dth complexes the same as in $[M(H_2O)_n]^{2+}$. These effects are not pronounced in the ternary complexes of trp containing mixed donor sites (N and O). Hence, the values of Δ log K_M were found to be negative. Such results have also been observed by Sigel and Griesser[14]. The positive values of Δ log K_M may also be due to the absence of coulombic repulsion between two dissimilar ligand bound to the same metal ion and the negative values are due to smaller coulombic attraction of secondary ligand (sal).

It is evident from the above discussion that the ternary complexes are stabilized by several factors. Besides these factors, intramolecular aromatic ring stacking also plays an important role in increasing the stability constants of ternary complexes[15]. Dithionon is a rigid as well as a good π-acceptor molecule while the ring system of trp is attached to a flexible side chain. Both of these ligands, when coordinated to the same metal ion, produce intramolecular aromatic ring stacking between the

aromatic ring systems of the two ligands. It is possible because the ring system of trp may reach easily to the rigid aromatic ring system of dth to produce these interactions. Such effects are less remarkable in the ternary complexes of sal and trp, because the ring system of sal is not rigid and there remains a freely hanging phenyl ring having no functional group that might involve in bonding. A tentative structure of stacked ternary complex of MAL^+ has been shown in Fig. 3. These results find

Fig. 3. A tentative structure of stacked ternary MAL^+ complex.

further support from the work of Sigel *et al*[15,16] on the intramolecular hydrophobic interactions in ternary complexes of some aliphatic amino acids and ring stacking in ternary complexes of some aromatic amino acids. Similar results were also observed in our previous investigation on the stacked ternary complexes of some plant auxins involving 2,2′-bipyridyl and 1,10-phenanthroline as primary ligands[17].

On the basis of considerably high stability constants of binary and ternary metal complexes reported here, the metal ions which are vital constituent of various enzymes may interact with fungicides forming binary complexes which are further converted into ternary complexes involving tryptophan. Thus, all the enzymatic equilibria are disturbed and the conversion of tryptophan into various products is inhibited causing growth regulation.

Acknowledgement

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Stabilisation of Molybdenyl Cations with 4,4′-Dimethyl 2,2-Bipyridyl in Different Salt and Non-electrolytic Complexes

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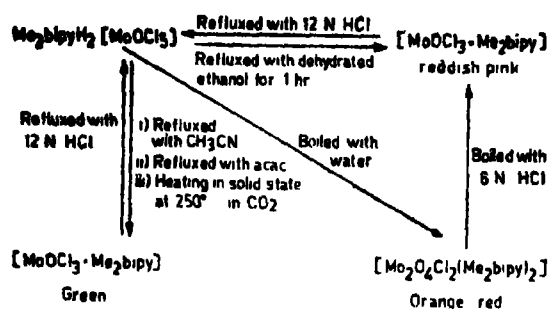
The aqueous chemistry of molybdenyl cation MoO^{3+} has been studied. The heterocyclic base 4,4′-dimethyl 2,2′-bipyridyl has been shown to function as diacidic base in strong hydrochloric acid medium to yield the salt $Me_2bipyH_2[MoOCl_5]$. The non-electrolytic complexes $[Mo_2O_4Cl_2(Me_2bipy)_2]$ and $[MoOCl_3.Me_2bipy]$ have been isolated from the parent salt by hydrolytic and dehydrohalogenation reaction in solution and in solid state.

THE effect of substitution in 1,10-phenanthroline and 2,2′-bipyridyl on the complexation of metal ions has been studied only in some isolated cases. It is known that 1,10-phenanthroline gives stable complex with iron, but, 2,9-dimethyl 1,10-phenanthroline fails to do this due to steric factor. Identical observations have been reported by the present author in the case of molybdenyl cation also. The similarity of MoO^{3+} with Fe^{3+} ion in high spin state has also been established[1].

In the present investigation the role of 4,4′-dimethyl 2,2′-bipyridyl in the aqueous chemistry of molybdenyl cation has been fully investigated. The salt $Me_2bipyH_2[MoOCl_5]$ and the non-electrolytic complexes $[MoOCl_3.Me_2bipy]$ (in two forms, reddish pink and green varieties) and $[Mo_2O_4Cl_2(Me_2bipy)_2]$, isolated in pure state by the present authors, have been thoroughly studied by analytical and different physico-chemical methods. The interconversion of the products and reactants is shown below which establishes the stability of the "oxometal" entity MoO^{3+} in different chemical reactions.

Experimental

All reagents used were of A. R. grade. Molybdenum was estimated gravimetrically as molybdenum trioxide and chlorine was estimated as silver chloride[2]. Nitrogen was estimated by Duma's method. The oxidation state of the metal was determined by ceric sulphate method.

4,4-′Dimethyl 2,2′-bipyridinium oxopentachloro molybdate(V), $Me_2bipyH_2[MoOCl_5]$: This anhydrous salt was prepared by reducing MoO_3 (2 g) with HI (2 ml) in hydrochloric acid (12 *N*) medium and the green crystalline salt was obtained by adding 2 g of the base, yield 5.3 g. (Found : Mo, 20.18; Cl, 37.68; N, 5.89. Calcd. for $Me_2bipyH_2[MoOCl_5]$; Mo, 20.20; Cl, 37.20; N, 5.88%). Oxidation state of the metal was found to be 4.99.

Oxotrichloro(4,4′-dimethyl 2,2′-bipyridyl) molybdenum(V), $MoOCl_3.Me_2bipy$ (reddish pink) : Dehydrohalogenation was effected by refluxing 1 g of 4,4′-dimethyl 2,2′-bipyridinium oxopentachloromolybdate(V) with 20 ml of dehydrated ethanol for about 1 hr under positive pressure of the solvent. The pink product was filtered, washed and dried in a vacuum desiccator, yield about 0.7 g. (Found : Mo, 23.49; Cl, 26.93; N, 7.47. Calcd. for $MoOCl_3.Me_2bipy$; Mo, 23.85; Cl, 26.45; N, 6.95%). The oxidation state of the metal was found to be 5.0.

Oxotrichloro(4,4′-dimethyl 2,2′-bipyridyl)molybdenum(V), $MoOCl_3.Me_2bipy$ (green) : A sample of about 1 g of the parent salt $Me_2bipyH_2[MoOCl_5]$ was refluxed with 15 ml acetonitrile for 3-4 hr. The evolved gas contained hydrogen chloride. The bright green crystalline solid so formed was filtered and dried in a vacuum desiccator, yield about 0.65 g. (Found : Mo, 23.69; Cl, 27.14; N, 7.12. Calcd. for $MoOCl_3.Me_2bipy$; Mo, 23.85; Cl, 26.45; N, 6.95%). The oxidation state of the metal was found to be 5.09.

Alternatively, the green compound can also be prepared by refluxing the parent salt with acetylacetone or heating the parent salt in solid state at 250° for 2 hr in CO_2 atmosphere.

Oxo-μ-dioxochloro(4,4′-dimethyl 2,2′-bipyridyl) molybdenum(V), $[Mo_2O_4Cl_2(Me_2bipy)_2]$: Hydrolysis of the parent salt (1 g) was effected by boiling with distilled water when the orange red solid separated. It was cooled, filtered in a sintered gooch crucible, washed with cold water and dried

in vacuum desiccator, yield 0.75 g. [Found : Mo, 27.44 ; Cl, 10.02 ; N, 8.04. Calcd. for $Mo_2O_4Cl_2$-$(Me_2bipy)_2$; Mo, 27.62 ; Cl, 10.21 ; N, 8.05%]. The oxidation state of the metal was found to be 5.04.

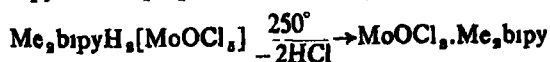
This compound is isoluble in water and common organic solvents. Boiling it with 6 *N* hydrochloric acid produces the reddish pink $MoOCl_3.Me_2bipy$.

Conductivity measurements : The extensive hydrolysis and ionisation of the oxopentahalomolybdate(V) ion was confirmed by conductance measurement of the salts in aqueous medium. The non-electrolytic nature of $MoOX_3$.L type of compounds was established by conductance measurements in acetonitrile. The conductance values in 10^{-3} *M* solution, of the reddish pink and the green forms of $[MoOX_3.Me_2bipy]$ are 5.02 and 5.26 $ohm^{-1}cm^2 mole^{-1}$, respectively which are much less than those for binary electrolytes[8] (the conductivity of a 1 : 1 electrolyte in $10^{-3}M$ solution ranges from 120-160 $ohm^{-1}cm^2mole^{-1}$). Since the hydrolytic product $Mo_2O_4Cl_2(Mebipy)_2$ is practically insoluble in almost all solvents, conductance measurement was not possible.

Measurement of magnetic susceptibility : Magnetic susceptibility measurements of the compounds were carried out at room temperature using Gouy balance having a field strength of 8500 gauss and the values of effective moments were found using the formula $\mu_{eff}=2.839\ (\chi'_M.T)^{\frac{1}{2}}$ where χ'_M is the molar susceptibility after diamagnetic correction. The μ_{eff} values of the compounds Me_2bipyH_2-$[MoOCl_5]$, $MoOCl_3.Me_2bipy$ (reddish pink), $MoOCl_3.Me_2bipy$ (green) and $Mo_2O_4Cl_2(Me_2bipy)_2$ are 1.81, 1.81, 1.88 and 0.52 B.M., respectively.

It appears from the results of magnetic susceptibility measurements that the salt Me_2bipyH_2-$[MoOCl_5]$ and both varieties of the mononuclear complex $MoOCl_3.Me_2bipy$ contain quinquevalent molybdenum having d^1 configuration. The hydrolytic product $Mo_2O_4Cl_2(Me_2bipy)_2$ has a small magnetic moment due to oxobridges with a possible Mo-Mo interaction.

Thermogravimetry Thermogravimetric investigations were made in a T. G. Analyser of Cieco Pvt. Co. The results are plotted in Fig. 1. It appears that at 250° the stable state corresponds to the weight loss of 15.11%, whereas the theoretical weight loss according to the following thermal dehydrohalogenation is 15.35%. Therefore, the non-electrolytic paramagnetic derivative $MoOCl_3.Me_2$-bipy can be prepared at this temperature.

$$Me_2bipyH_2[MoOCl_5]\ \xrightarrow[-2HCl]{250^\circ} MoOCl_3.Me_2bipy$$

At 570°, the total weight loss is 70.36% which is in excellent agreement with the formation of MoO_3 which requires a theoretical weight loss of 69.69%. The synthesis of $MoOCl_3.Me_2bipy$ by thermal

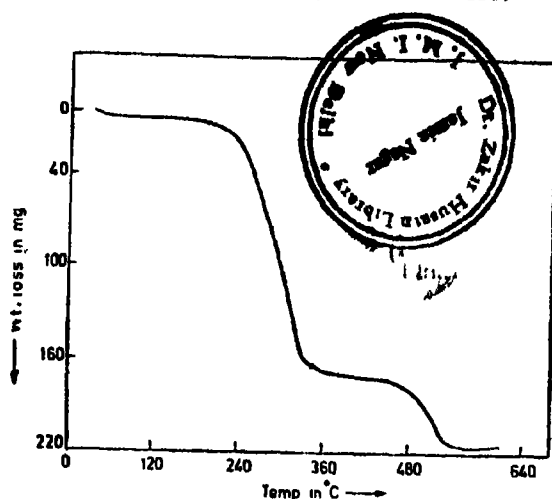



Fig. 1. TGA Diagram of $Me_2bipyH_2[MoOCl_5]$

dehydrohalogenation of the salt Me_2bipyH_2-$[MoOCl_5]$ has been mentioned which also confirms the thermogravimetric analysis of the compound.

IR spectra : Infrared spectra were recorded in Perkin-Elmer IR spectrophotometer using KBr pellet The ir spectrum of the salt Me_2bipyH_2-$[MoOCl_5]$ shows a strong absorption band at 980 cm^{-1} while for the two isomers it appears at 960 cm^{-1} (*cis*) and 965 cm^{-1} (*trans*), respectively. The hydrolysed product $Mo_2O_4Cl_2(Me_2bipy)_2$ shows strong absorption at 945 cm^{-1}. These bands can be assigned to the molybdenum oxygen stretching frequency, indicating the presence of Mo(V)=O species in all the compounds.

Examination of the stretching frequencies indicates that there is a gradual decrease in metal-oxygen bond strength from $Me_2bipyH_2[MoOCl_5]$ to hydrolysed product, as the chlorine atom is replaced by a nitrogen atom (from 4,4'-dimethyl 2,2'-bipyridyl) and an oxygen atom (forming an oxobridge) causing a reduction in the value of the stretching frequency. This is probably due to the strong donating capabilities of the nitrogen atoms of Me_2bipy and oxygen of oxobridge, causing increased electron density around the central metal atom and thereby reducing its π-acceptance capacity and ultimately the metal-oxygen bond strength. The broader bands in the region 700-800 cm^{-1} in the case of hydrolytic product may be assigned to metal oxygen chain (–Mo–O–Mo–O) vibrations.

UV and visible spectra : UV and visible spectra were recorded on a Hilger Uvispek spectrophotometer. The solvent used in the case of the salt was 10 *M* hydrochloric acid and in the case of both the isomeric varieties of $MoOCl_3.Me_2bipy$, it was acetonitrile (A.R.). As the hydrolytic product is insoluble in common organic solvents, its reflectance spectrum was taken in the solid state using spectrochemically pure liquid paraffin. Reflectance spectra were also taken for the two isomers of $MoOCl_3.Me_2bipy$. The absorption bands together

TABLE 1—ELECTRONIC SPECTRA OF THE SALT AND NON-ELECTROLYTIC ISOMERS

Compound	λ_{max} mμ	ν(cm$^{-1}\times 10^{-3}$)	Molar extinction coefficient ϵ	Assignment
Me$_2$bipyH$_2$[MoOCl$_5$] in 10 *M* HCl	700	14.29	13.50	$^2B_2\rightarrow{}^2E$ (I)
	440	22.72	15.04	$^2B_2\rightarrow{}^2B_1$
	370	27.03	207 00	$^2B_2\rightarrow{}^2E$ (II)
	295	33.90	15,450	$^2B_2\rightarrow{}^2B_2$ (I)
	232	43 10	12,000	$^2B_2\rightarrow{}^2E$ (III)
[MoOCl$_3$.Me$_2$bipy] (reddish pink) in acetonitrile	740	13.51	90.00	$^2B_2\rightarrow{}^2E$ (I)
	520	19.23	708.00	L $\rightarrow$Mo Charge transfer
	430	23.25	504.00	$^2B_2\rightarrow{}^2B_1$
	370	27.03	900.00	$^2B_2\rightarrow B_2$ (I)
[MoOCl$_3$.Me$_2$bipy] (green)	750	13.33	65.00	$^2B_2\rightarrow{}^2E$ (I)
	530	19.23	125.00	L $\rightarrow$ Mo Charge transfer
	375	26.67	600.00	$^2B_2\rightarrow{}^2B_1$
	305	32.78	10,900	$^2B_2\rightarrow{}^2B_2$ (I)
	240	41.67	15 800	$^2B_2\rightarrow{}^2E$ (III)

with molar extinction coefficient and the corresponding intensities in the case of reflectance spectra and their tentative assignments are given in Tables 1 and 2. The results clearly agree with previous observations[4,5].

TABLE 2—REFLECTANCE SPECTRA IN SOLID STATE

Compound	ν(cm$^{-1}\times 10^{-3}$)	Intensities	Assignment
MoOCl$_3$.Me$_2$bipy (reddish pink)	13.50	s	$^2B_2\rightarrow{}^2E$ (I)
	19.60	sh	L $\rightarrow$Mo Charge transfer
	22.90	m	$^2B_2\rightarrow{}^2B_1$
	25.80	sh	$^2B_2\rightarrow{}^2B_2$ (I)
MoOC$_3$.Me$_2$bipy (green)	14 00	m	$^2B_2\rightarrow{}^2E$ (I)
	18.90	w	L $\rightarrow$ Mo Charge transfer
	23.40	sh	$^2B_2\rightarrow{}^2B_1$
	26.00	m	$^2B_2\rightarrow 2B_2$(I)
Mo$_2$O$_4$Cl$_2$(Me$_2$bipy)$_2$	11.50	m	$^2B_2\rightarrow{}^2E$ (I)
	17.50	sh	L $\rightarrow$ Mo Charge transfer
	22.90	sb	$^2B_2\rightarrow{}^2B_1$
	26.20	m	$^2B_2\rightarrow{}^2B_2$ (I)

s=strong ; m=medium , sh=shoulder , sb=strong broad.

Results and Discussion

The $MoOCl_5^{2-}$ ion is visualised as a tetragonal structure with a short Mo–O bond having C_{4v} symmetry[6]. The expected transitions with identical scheme agree very closely with the experimental results. The salt 4,4'-dimethyl 2,2'-bipyridinium oxopentachloromolybdate(V) in 10 *M* HCl shows two crystal field transitions $^2B_2\rightarrow{}^2E$ (I) and $^2B_2\rightarrow{}^2B_1$ at 14,290 and 22,720 cm^{-1} and three charge transfer transitions $^2B_2\rightarrow{}^2E$ (II), $^2B_2\rightarrow{}^2B_1$ (I) and $^2B_2\rightarrow{}^2E$ (III) at 27,030, 33,900 and 43,100 cm^{-1}, respectively. About the monomeric complex [MoOCl$_3$.Me$_2$bipy], the molecular orbital picture is expected to be different. In this case the number of symmetry elements is expected to be less than that in the case of $MoOCl_5^{2-}$ ion which belongs to C_{4v} point group. But the other distortions from octahedral structure compared to the distortion caused by Mo–O interaction are expected to be moderate. There may be considerable π-interaction with the filled π-orbitals of the ligand and metal d-orbitals. Therefore, a red shift is logical consequence of this effect and this has actually happened in this case as the following ν-values of the first crystals field transition reveal.

	Compound	ν in cm$^{-1}\times 10^{-3}$
(a)	Me$_2$bipyH$_2$[MoOCl$_5$]	14.29
(b)	[MoOCl$_3$.Me$_2$bipy] (reddish pink)	13.51
(c)	[MoOCl$_3$.Me$_2$bipy] (green)	13.33

The solution and reflectance spectrum of the two isomeric forms of [MoOCl$_3$.Me$_2$bipy] are similar. A new band appears in the region 19,000 cm^{-1} which may be due to a Me$_2$bipy$\rightarrow$Mo charge transfer transition. In the case of Mo$_2$O$_4$Cl$_2$(Me$_2$bipy)$_2$, the L$\rightarrow$Mo charge transfer band has undergone a red shift compared to the mononuclear complex [MoOCl$_3$.Me$_2$bipy], as the chlorine atom has been replaced by oxygen (forming bridge) which is expected to reduced the Mo-ligand bond strength.

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Synthesis and Structural Studies of the Complexes of Zn(II), Ni(II), Cu(II) and Co(II) with 3-Aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazoles

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Complexes of Zn(II), Cu(II), Ni(II) and Co(II) with 3-aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazoles have been prepared. They have been characterised on the basis of elemental analyses, infrared spectra, thermogravimetry, magnetic susceptibility and powder X-ray diffraction patterns. Fungitoxicity of the complexes and free ligands has been evaluated against *H. orysae* X-ray studies reveal that the complexes possess cubic structure.

COMPOUNDS containing triazole ring have been reported to have bactericidal[1,2], fungicidal[3,4], insecticidal[5,6] and pesticidal[7,8] properties. 3-Amino-1,2,4-triazole (Amizole) is a commercial herbicide. Importance of metal complexes has also been established and some of them are found to possess biological activity. Some drugs have increased activity when administered as metal complexes[9] and a number of metal chelates inhibit tumour growth. The complexes of Co(II) and Cu(II) with 3-methyl-4-(2-pyridyl)-1,2,4-triazole-5-thiol have been reported[10]. The present communication reports the synthesis and charaterisation of Zn(II), Co(II), Cu(II) and Ni(II) complexes with 3-aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazoles.

Experimental

All chemicals used were of B. D. H. grade or of equivalent quality.

Preparation of 3-aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazole : A mixture of an aryloxyacetylhydrazine (0.01 *M*) and arylisothiocyanate (0.012 *M*) was refluxed in NaOH solution (20 ml ; 8%) for 5 to 6 hr when a clear solution resulted. It was cooled, poured into water and filtered. The filtrate on acidification gave a precipitate which was filtered, washed and recrystallised. The compounds, thus prepared, were characterised by elemental analysis and ir spectra (Table 1).

Preparation of metal complexes : The complexes were precipitated by refluxing a methanolic solution of 3-aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazole (0.01 *M*) with aqueous solution of a metal salt (0.03 *M*) for 4 to 6 hr. The precipitate was filtered, washed successively with large excess of water, hot methanol, ether and dried *in vacuo*.

Analyses of the metal complexes : Metal ions in the complexes were estimated by the methods in literature[11]. The metal complexes were also analysed for their metal contents as their oxides. For this purpose, weighed samples in silica crucible were first gently heated on a naked flame for 1 hr and then in an electric furnace at 800±10° to a constant weight. These were cooled and weighed. Sulphur and nitrogen were estimated by the usual methods (Table 1).

TABLE 1—3-ARYLOXYMETHYL-4-ARYL-5-MERCAPTO-1,2,4-TRIAZOLES

Sl No	R	m.p. °C	N% Found (Calcd.)	S% Found (Calcd.)
1	2-CH_3-C_6H_4-$OCH_2$$^-$	178	13.92 (14.14)	10.92 (10.77)
2.	2-Cl-C_6H_4-$OCH_2$$^-$	183	13 82 (13 20)	10.74 (10.06)
3.	*4-Cl-C_6H_4-$OCH_2$$^-$	160	12.94 (13 20)	10 88 (10.06)

IR Spectral Data ν_{max} in cm^{-1}

*Conjugated >C=N	p-disubstituted benzene	monosubstituted benzene	C=S	>C-O-C<
1740	830	770	1175	1260

Physical measurements : The magnetic susceptibilities of the complexes were determined by Faraday method using ferrous ammonium sulphate as calibrant. Experimental magnetic susceptibilities were corrected for diamagnetism[12]. The magnetic moments of the complexes at room temperature are given in Table 2.

The ir spectra of the complexes and the ligand were recorded on a Perkin-Elmer spectrophotometer, Model 621, in KBr phase in 4000-200 cm^{-1} range.

TABLE 2—ANALYTICAL DATA AND MAGNETIC MOMENTS OF THE COMPLEXES

Complex composition	Metal % Found (Calcd.)	N% Found (Calcd.)	μ_{eff} B.M. Found (Calcd)
$[ZnL_2(Ac)_2]$	8.80 (8.86)	10.21 (10.61)	Diamagnetic
$[ZnL_4]Cl_2$	4.8 (4.90)	13.3 (12.68)	Diamagnetic
$[CuL_2(Ac)_2].H_2O$	7.3 (7.60)	10 8 (10.45)	1.18 (1.73)
$[Ni(NO_3)_2L_2.2H_2O]$	6.9 (6.86)	12.9 (13 10)	2.97 (2.83)
$[Co(NO_3)_2L_4]$	4.2 (4.05)	10 2 (10.84)	3.94 (3.87)

TABLE 3—CRYSTAL DATA FOR THE COMPLEXES

Complex	Lattice parameter and lattice type
$[ZnL_2(Ac)_2]$	a = 20 6Å Cubic
$[CuL_2(Ac)_2]H_2O$	a = 17.70Å Cubic
$[Ni(NO_3)_2L_2\ 2H_2O]$	a = 18 69Å Cubic
$[Co(NO_3)_2L_4]$	a = 21.38Å Cubic

The thermogravimetry of the complexes were carried out with the help of a manual thermogravimetric analyser (supplied by P & D Division, FCI Ltd., Sindri) at a heating rate of 4° min^{-1} in air. Results are recorded in Table 4.

TABLE 4—TG DATA FOR METAL COMPLEXES

Stable phase or thermal decomposition	Temp. range (°C)	%wt loss Found (Calcd.)
$ZnL_2(Ac)_2$	60-300	8.53 (7.69)
$ZnL_2(Ac)_2$	300-540	46 85 (46 20)
$ZnL(Ac)$	540-700	88.83 (89.67)
ZnO		
ZnL_4Cl_2	140-340	43 29 (44 86)
ZnL_2Cl_2	310-700	90 90 (89.72)
$ZnCl_2$		
$CuL'_2(Ac)_2.H_2O$	80-160	1 90 (2.15)
$CuL_2(Ac)_2$	160-460	47.908 (47.27)
$CuL(Ac)$	460-700	87.95 (90.48)
CuO		
$Ni(NO_3)_2.L_2.2H_2O$	80-120	4 76 (4.21)
$Ni(NO_3)_2L_2$	120-360	42.77 (41.41)
$Ni(NO_3)_2L$	360-660	93.56 (91.26)
NiO		
$Co(NO_3)_2L_4$	80-320	42.0 (43.71)
$Co(NO_3)_2L_2$	320-460	66.6 (65.56)
$Co(NO_3)_2L$	460-700	96.0 (94.84)
CoO		

Powder X-ray diffraction patterns of the complexes were taken, using CuK radiation, employing a Guinier camera of 11.46 cm diam and X-ray unit of PW 1011 Philips, Holland. The diffraction patterns were indexed by Hessé-Lipson method. The agreement between the observed and calculated values of $\sin^2\theta_{hkl}$ was satisfactory which indicated that the indexing was correct.

Fungitoxicity of the complexes and the ligands were also evaluated against *H. oryzae* by agar-plate method[13] at three different concentrations. The average per cent inhibition (Table 5) by various complexes were calculated by the expression :

$$\text{Per cent inhibition} = \frac{(C-T)\times 100}{C}$$

where C = diameter of the fungus colony in the control plate after 96 hr and T = diameter of the fungus colony in treated plates after 96 hr.

TABLE 5—FUNGICIDAL SCREENING

(Organism—*H. oryzae*)

Average Percent Inhibition after 96 hr

	Concentration 1 : 1,000	1 : 10,000	1 : 100,000
Zinc acetate complex	56 2	30 25	10.09
Zinc chloride complex	55.4	27 28	9 98
Ligand for the above complexes	44 9	21.30	11.05
Cobalt nitrate complex	45 2	22 75	12.54
Nickel nitrate complex	43.2	20.24	12 00
Ligand for the above complexes	38.9	19.25	9 25
Copper acetate complex	57.3	28 35	11.55
Ligand for the above complex	45.8	20.00	10.50

Results and Discussion

The zinc complexes are found diamagnetic as expected The structure proposed for the complexes is also in accordance with the diamagnetic behaviour The magnetic moment value of Cu(II) acetate complex is found to be 1.18 B.M. This low value of magnetic moment could be explained by spin-spin interaction between two cupric ions, which is usually observed in other Cu(II) acetate complexes[14]. The magnetic moment value (2.97 B.M.) for Ni(II) complex lies well within the range accepted for the octahedral complexes of this metal ion[15]. The value of magnetic moment (3.94 B.M.) for Co(II) complexes is well within the range accepted for Co(II) complexes having three unpaired electrons.

The infrared spectra of ligands 3-tolyloxymethyl-4-aryl-5-mercapto-1,2,4-triazole, 3-(*p*-chlorophenoxy)methyl-4-aryl-5-mercapto-1,2,4-triazole and 3-(*o*-chlorophenoxy)methyl-4-aryl-5-mercapto-1,2,4-triazole show bands at 3500, 3040 cm^{-1} ; 3420, 3050 cm^{-1} and 3412, 3025 cm^{-1}, respectively which may be assigned to ν_{asym}N–H and ν_{sym} N–H vibrations, respectively. A weak band in the region 2550-2600 cm^{-1} in the spectra of these ligands may be assigned as ν_{S-H} stretching vibration. The bands observed at 1120, 1175 and 1060 cm^{-1} in the spectra of the respective ligands are

due to $>$C=S stretch. The ligand spectra show bands due to conjugated $>$C=N, *o*- and *p*-disubstituted benzene rings at 1735-1740, 960-1040 and 800-855 cm^{-1}, respectively. It may be concluded from these that the ligand exists in the following tautomeric form :

Thiol form ⇌ Thione form

An analysis of the spectra of the complexes and their respective ligands shows that ν_{S-H} band in the region 2550-2600 cm^{-1} is absent in the spectra of the complexes whereas the ν_{N-H} band is present. Further, there is a strong negative shift in ν_{C-S} band in 1050-1200 cm^{-1} region. These clearly indicate that the thione form is favoured for complexation, coordination takes place through S atom of the thione and the ligands act as monodentate.

The assymmetric and symmetric $>$C=O stretching frequencies of free acetate ion observed at 1578 and 1425 cm^{-1}, respectively are observed at 1595 and 1430 cm^{-1}, respectively in Zn(II) acetate complex and at 1610 and 1440 cm^{-1} in Cu(II) acetate complex. A separation of about 165 and 160 cm^{-1} in the above modes in Zn(II) and Cu(II) acetate complexes suggests that the acetate group behaves as monodentate ligand in these complexes[16]. In Cu(II) acetate complex there is a band at 3560 cm^{-1} which is due to the presence of lattice water.

In case of Ni(II) and Co(II) nitrate complexes the presence of two bands at 1500, 1270 cm^{-1} and 1495, 1275 cm^{-1}, respectively due to ν_s of nitrato group, indicates that the nitrate ion behaves as a monodentate ligand[17].

Crystal data reported in Table 3 indicate that the crystal lattice of all the complexes belongs to cubic system. The lattice parameter of the complexes are also shown.

On the basis of thermoanalytical data, the mechanism of decomposition of complexes has been proposed and is shown in Table 4. The decomposition products of all the complexes were analysed and the end products were found to be respective metal oxides except for zinc chloride complex. From the TG data it is clear that the mass loss starts at about 80°. The mass loss at a low rate right from the start may be due to desorption of adsorbed gases or moisture.

Fungicidal screening data (Table 5) indicate that the complexes are more fungitoxic than free ligand.

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Coordination Polymers of Terephthalaldehyde bis-(semicarbazone) with Some Bipositive Cations

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Terephthalaldehyde *bis*-(semicarbazone) forms polymeric metal complexes, -(-ML.2H$_2$O-)-$_n$ [where M=Mn(II) Co(II) Ni(II), Cu(II) or Zn(II), and L=C$_{10}$H$_{10}$N$_6$O$_2$], which are coloured, powdery, air stable and insoluble in water and common organic solvents The composition, structure and thermal stability of the complexes have been discussed on the basis of the results of analytical, magnetic, spectral (ir and drs) and thermogravimetric studies.

Terephthalaldehyde *bis*-(semicarbazone) acts as a tetradentate chelating agent, coordinating in enolic form. The coordination takes place through the enolic oxygens and azomethine nitrogens, and polymeric complexes are formed as the steric factors prevent the coordination of all the donors to the same metal ion. The complexes have octahedral geometry, and the order of thermal stability is Zn > Ni > Co > Mn > Cu.

IN continuation of our earlier work[1-4] on coordination polymers of terephthalaldehyde derivatives, the present investigation was undertaken to isolate polymeric metal complexes of terephthalaldehyde *bis*-(semicarbazone) (TBSC) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The analytical, magnetic, spectral (ir and drs) and thermogravimetric studies of the complexes are being described.

Experimental

Materials : Terephthalaldehyde *bis*-(semicarbazone) was prepared by the reported method[5]. The solvents and metal salts used were as described earlier[4].

Preparation of the complexes : 2.48 g (0.01 *M*) TBSC dissolved in DMSO was added to a metal salt solution (0 01 *M*) [containing 1 98 g of $MnCl_2.4H_2O$, 2.49 g of $Co(CH_3COO)_2.4H_2O$, 2 49 g of $Ni(CH_3COO)_2.4H_2O$, 2 00 g of $Cu(CH_3COO)_2.H_2O$ or 2.20 g of $Zn(CH_3COO)_2.2H_2O$] in DMSO. The mixture was stirred and refluxed on a sand bath for *ca* 2 hr and left overnight. The resulting solid was filtered, washed successively with DMSO, ethanol, hot water and ether and dried.

The complexes are coloured, powdery, air stable and insoluble in water and common organic solvents viz. ethanol, acetone, benzene, chloroform, nitrobenzene, carbon tetrachloride, THF, DMF and DMSO. The physico-chemical measurements were done as described earlier[1].

Results and Discussion

The analytical data of the complexes (Table 1) agree with the general formula -(-ML.2H$_2$O$_n$-)- [where M=Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) ; L=C$_{10}$H$_{10}$N$_6$O$_2$].

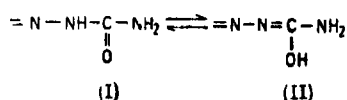
TABLE 1 – ANALYTICAL DATA OF THE COMPLEXES

Empirical formula	Colour	Analysis % Found (Calcd)			
		Metal	C	H	N
MnL.2H$_2$O	Yellow	15.86 (16.32)	35.04 (35.60)	4.68 (4 16)	24.27 (24.92)
CoL.2H$_2$O	Red	17.86 (17.30)	34.95 (35.15)	4.17 (4.10)	24.80 (24.68)
NiL.2H$_2$O	Yellow	17.00 (17.20)	34.40 (35.23)	4.35 (4.11)	24.48 (24.65)
CuL 2H$_2$O	Greenish yellow	17 79 (18.38)	34 88 (34.78)	4.08 (4.06)	23.93 (24.31)
ZnL.2H$_2$O	Yellow	17.28 (17.89)	32.49 (32.85)	3 67 (3 83)	22.56 (22.99)

L=C$_{10}$H$_{10}$N$_6$O$_2$

Semicarbazones (=N–NH–CO–NH$_2$) exhibit tautomerism due to the presence of C=O group in the neighbourhood of NH, H being enolizable. Thus, semicarbazones may coordinate with metals in both keto (I) or enolic (II) form.

$$=N-NH-\underset{\underset{O}{\|}}{C}-NH_2 \rightleftharpoons =N-N=\underset{\underset{OH}{|}}{C}-NH_2$$

(I) (II)

The ir spectrum (wave numbers in cm^{-1}) of TBSC (Table 2) shows the band at 3140 assignable to NH stretching The bands appearing at 1670, 1645 and 1590 are due to C=O, C=N and C=C stretching frequencies, respectively The mixed NH$_2$ deformation and C–N stretching frequency, N–N stretching, and C=O in-plane deformation bands occur at 1510, 925 and 750, respectively. These observations indicate that TBSC in solid state exists in keto form[6].

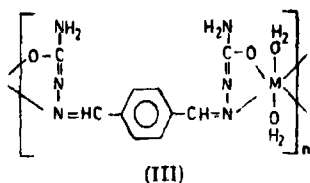
In the spectra of the complexes, C=O stretching band disappears and new bands appearing at 1570-1550 and 1290-1285 are assigned to C=N–N=C stretching and C–O stretching at C–O–M

* For correspondence.

TABLE 2—CHARACTERISTIC BANDS OF IR SPECTRA OF TBSC AND ITS COMPLEXES

TBSC	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Assignment
...	3450	3360	3480	3460	3400	3420	νO−H
3140	3120	3100	3120	3120	3110	3120	νN−H
3020	3000	2980	3020	3020	3020	2990	νC−H
1670	...	...	...	...	...	...	νC=O
...	1680	1695	1685	1680	1685	1680	δH_2O
1645	1630	1630	1635	1640	1630	1635	νC=N
...	1570	1550	1550	1560	1550	1560	νC=N−N=C
1510	1520	1510	1510	1520	1510	1515	νC−N +δN−H
...	1280	1290	1290	1280	1285	1285	νC−O
...	520	520	515	515	510	520	νM−O
...	455	460	455	465	460	450	νM−N

site, respectively, indicating coordination of the ligand in enolic form to the metals. A negative shift in the stretching frequency of C=N (azomethine) group suggests the coordination of azomethine nitrogens. The coordination of azomethine nitrogen is also supported by a positive shift in the stretching vibrations of N−N group[7] in the spectra of the complexes. The coordination through oxygen and nitrogen is further confirmed by the occurrence of new bands at *ca* 520-510 and 460-450 in the spectra of the complexes, which may be assigned to M−O and M−N stretching frequencies, respectively[8]. The strong bands observed in the complexes in the region 3500-3300 and *ca* 1960 may be assigned to ν OH(H_2O) and δ H_2O respectively, and indicate the presence of lattice and/or crystallization and/or coordination water in the complexes[9].

(III)

Thus, the TBSC acts as tetradentate chelating agent, coordinating through the enolic oxygens and azomethine nitrogens, and polymeric complexes are formed (structure III) as the steric factors prevent the coordination of all the donor groups to the same metal ion.

TBSC is yellow in colour and therefore severely restricts the utility and accuracy of the electronic spectral studies, since intraligand bands interfere with the d-d bands of transition metal ions in the electronic spectra of the complexes.

The drs of TBSC shows strong band with its λ_{max} at 380 nm (26,300 cm^{-1}) with a minor peak on the lower wavelength side at 270 nm (37,000 cm^{-1}). On the higher side absorption decreases more rapidly but it does not disappear up to 840 nm. The bands in the ligand may be assigned to the intraligand transitions, $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$.

The observed magnetic moment of Mn(II)-complex is 5.89 B.M. which is in accordance with the value expected for spin only value for five unpaired electrons in an octahedral Mn(II)-complex involving sp^3d^2 hybridization. The reflectance spectrum shows weak bands at 16,130, 21,740, 27,780, 29,410 and 31,000 cm^{-1}. The three higher bands have been assigned to $^6A_{1g}\rightarrow{}^4T_{1g}$ (G), $^6A_{1g}\rightarrow{}^4T_{2g}$ (G) and $^6A_{1g}\rightarrow{}^4E_g$ (G) and the two lower bands to the transitions $^6A_{1g}\rightarrow{}^4T_{2g}$ (D) and $^6A_{1g}\rightarrow{}^4E_g$ (D) respectively, in an octahedral field of Mn(II) ion[10,11].

The observed magnetic moment of Co(II)-complex is 4.87 B.M. In drs of Co(II)-complex, two bands appear at 10,000 and 22,900 cm^{-1} which may be assigned to $^4T_{1g}$ (F)$\rightarrow{}^4T_{2g}$ (F) (ν_1) and $^4T_{1g}$ (F)$\rightarrow{}^4T_{1g}$ (P) (ν_3). However, the $^4T_{1g}$ (F) $\rightarrow{}^4A_{2g}$ (F) (ν_2) transition is not observed, since it is a two electron process and has a much lower oscillator strength than the other two transitions, and is therefore much weaker. The values of 10 Dq and ν_2 have been calculated to be 11,350 and 21,350 cm^{-1}, respectively The ν_2/ν_1 ratio, which is found to be 2.13, lies within the limit (2.1-2.2) reported for octahedral Co(II)-complexes[12].

The electronic spectrum of Ni(II)-complex shows three d-d transition bands at 10,526, 15,652 and 26,319 cm^{-1} which correspond to the transitions $^3A_{2g}\rightarrow{}^3T_{2g}$ (F) (ν_1), $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) (ν_2) and $^3A_{2g}\rightarrow{}^3T_{1g}$ (P) (ν_3), respectively. The ν_2/ν_1 ratio is 1.50 The magnetic moment value (2.94 B.M.) together with drs data shows the octahedral geometry of Ni(II)-complex.

Cu(II)-complex has a magnetic moment value of 1.79 B.M. The electronic configuration $3d^9$ gives rise to ^2D free ion term which splits in a regular octahedral environment into a lower doublet ^2E_g and an upper triplet $^2T_{2g}$ levels. In electronic spectrum, only one band due to $^2E_g\rightarrow{}^2T_{2g}$ transition is expected but true octahedral structures are uncommon. Here, three bands appear as shoulders at 10,000, 11,110 and 15,150 cm^{-1} which may be assigned to $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2B_{2g}$ and $^2B_{1g}\rightarrow{}^2E_g$ transitions, respectively in a distorted octahedral geometry of Cu(II) ion[14].

The thermal stability data of the complexes show that the initial weight loss is probably due to the loss of water molecules present in the complexes. The weight loss at the temperatures between 180-220° corresponds closely to water content of the chelates. On further heating, the organic component of the complexes decomposes leading to the formation of metal oxides. The order of thermal stability is Zn > Ni > Co > Mn > Cu.

The geometry of the ligand, composition, insolubility and thermal stability of complexes indicate that they are polymeric in nature[1-4].

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Stability and Related Thermodynamic of Chelation of Zn(II) with Thiodiacetic Acid (TDAA), Thiodipropionic Acid (TDPA), Iminodiacetic Acid (IDAA), Dithiodiacetic Acid (DTDAA) and Diglycolic Acid (DGA)

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The chelation of Zn(II) with TDAA, TDPA, IDAA, DTDAA and DGA has been studied potentiometrically in aqueous medium at different ionic concentrations (0.1, 0.2 and 0.3 *M* $NaClO_4$) and different temperatures (25, 35 and 45°) using Calvin-Bjerrum *p*H titration technique as modified by Irving and Rossotti. The thermodynamic stability constants and thermodynamic functions (ΔG, ΔH and ΔS) have been reported.

It appears from a survey of literature[1-4] that no effort has been made to determine the thermodynamic stability constants of the complexes formed by Zn^{2+} ions with TDAA, TDPA, IDAA, DTDAA and DGA. It was therefore considered of interest to study these systems potentiometrically. The thermodynamic stability constants of Zn(II) complexes were obtained by extrapolating the determined stability constants at various ionic strengths (0.1, 0.2 and 0.3 *M*; 25°) to zero ionic strength. The thermodynamic functions (ΔG, ΔH and ΔS) were also calculated at 0.1 *M*. The titration technique was that of Calvin and Wilson as modified by Irving and Rossotti[5-7].

Experimental

Materials: The solutions of TDAA, TDPA and DTDAA (Evan's Chematics), IDAA (Sigma Chem), DGA (John Backer Inc.) and zinc sulphate ($ZnSO_4.7H_2O$) were prepared in double distilled water. Perchloric acid (0.04 *M*) solution was prepared from the stock solution by dilution with double distilled water and standardized against standard NaOH solution. Other chemicals used were of A.R. grade. The stock solution of zinc sulphate was standardized gravimetrically as $ZnNH_4PO_4$.

Apparatus: A Philips *p*H meter (PR 9405 M) with glass and calomel electrodes assembly was used to measure the *p*H. The instrument was calibrated at *p*H 4.0 and 9.2 using buffer tablets.

Procedure: The experimental procedure used was the same as reported earlier[8]. The three solutions (total volume 50 ml in each case) were prepared as follows:

(i) 4×10^{-3} *M* perchloric acid,
(ii) 4×10^{-3} *M* perchloric acid+3×10^{-3} *M* ligand, and
(iii) 4×10^{-3} *M* perchloric acid+3×10^{-3} *M* ligand+5×10^{-4} *M* zinc ion solutions.

The concentration of the common ingradients in the solutions were identical in all the cases. An appropriate quantity of sodium perchlorate (0.2 *M*) was added to maintain the desired ionic concentrations of 0.1, 0.2 or 0.3 *M*. These solutions were titrated against a solution of 0.4 *M* caustic soda.

Results and Discussion

The *p*H range investigated for different systems were as follows:

System	*p*H range
Zn(II)-TDAA	2.9-5.4
Zn(II)-TDPA	4.1-5.0
Zn(II)-IDAA	5.3-7.8
Zn(II)-DTDAA	3.7-4.7
Zn(II)-DGA	2.4-3.5

The proton-ligand stability constants of TDAA, TDPA, IDAA, DTDAA and DGA and the stepwise formation constants of their chelates with Zn(II) were determined at 25±0.5°, 35±0.5° and 45±0.5° (Table 1) using Irving-Rossotti technique, and the values were further refined using the computational techniques[9,10], (i) curve fitting method and (ii) pointwise calculation method.

In Zn(II)-TDPA, Zn(II)-DTDAA and Zn(II)-DGA systems, the $\bar{n}$ values vary between 0.1 and 0.9, thereby indicating the formation of only 1 : 1 complex. In Zn(II)-TDAA and Zn(II)-IDAA, values of $\bar{n}$ vary between 0.2 and 1.9, indicating the formation of 1 : 1 as well as 1 : 2 complexes. The data in Table 1 reveal that stability constants decrease with increase in temperature and thus, lower temperature is favourable for complex formation. Metal-ligand stability constants increase with an increase in the ionic strength of the media. The thermodynamic stability constants (log $K_1^{\mu-0}$ and log $K_2^{\mu-0}$) have been evaluated at the standard state of infinite dilution and the values are given in Table 1.

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TABLE 1—PROTON-LIGAND STABILITY CONSTANTS OF TDAA, TDPA, IDAA, DTDAA AND DGA AND FORMATION CONSTANTS OF THEIR CHELATES WITH Zn(II)

Systems	Stability Constants	Temperature 25°C			35°C	45°C	25°C
		μ=0.1	μ=0.2	μ=0.3	μ=0.1	μ=0.1	μ=0.0
TDAA	Log K_1^H	4.33	4.25	4.18	4.22	4.17	4.40
	Log K_2^H	3.14	3.11	2.95	3.09	2.87	3.23
TDPA	Log K_1^H	4.80	4.83	4.86	4.61	4.51	4.77
	Log K_2^H	3.63	3.66	3.74	3.54	3.58	3.58
IDAA	Log K_1^H	9.36	9.25	9.05	8.88	8.79	9.51
	Log K_2^H	2.74	2.56	2.58	2.40	2.32	2.82
DTDAA	Log K_1^H	3.96	3.82	3.66	3.98	4.15	4.11
	Log K_2^H	2.82	2.66	2.62	2.83	2.88	2.92
DGA	Log K_1^H	4.05	3.94	3.84	4 06	4.18	4.15
	Log K_2^H	2.63	2 49	2 42	2 64	2 85	2.73
Zn(II)-TDAA	Log K_1	3 20	3.30	3 38	3.12	3.08	3.14
	Log K_2	2.67	2.70	2.76	2.66	2.65	2.62
Zn(II)-TDPA	Log K_1	3.01	3 11	3 20	2.97	2.94	2.91
Zn(II)-IDAA	Log K_1	5.95	6.82	7.70	5.92	5.89	5.08
	Log K_2	4.42	4.92	5.42	4.42	4.41	3.96
Zn(II)-DTDAA	Log K_1	2.73	2 93	3.15	2.72	2.70	2.52
Zn(II)-DGA	Log K_1	3.79	3.87	3.94	3.75	3.72	3.71

TABLE 2—THERMODYNAMIC PARAMETERS OF Zn(II) COMPLEXES (μ=0.1 *M*)

Ligand	Temp. °C	$-\Delta G$(Kcal.mole^{-1})		$-\Delta H$(Kcal mole^{-1})		ΔS(Cal.mole^{-1}.deg^{-1})	
		$-\Delta G_1$	$-\Delta G_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
	25	4.36	3 64				
TDAA	35	4.40	3.75	2.77	0 80	5.16	9.22
	45	4.48	3.86				
	25	4.11	—				
TDPA	35	4.19	—	1.47	—	8.57	—
	45	4.28	—				
	25	8.12	6.03				
IDAA	35	8.35	6 23	1.38	1.01	21.87	16.29
	45	8 57	6 42				
	25	3 72	—				
DTDAA	35	3.83	—	0.86	—	9.28	—
	45	3.93	—				
	25	5.17	—				
DGA	35	5.29	—	1.66	—	11.39	—
	45	5.42	—				

The thermodynamic functions ΔG, ΔH and ΔS were calculated at different temperatures using the standard equations[11] and are given in Table 2. ΔH values were calculated by plotting the values of log K_n at different temperatures as a function of (1/T) and equating the gradient of this plot with $-\Delta H/4.57$. Chelates of Zn(II) with TDAA, TDPA, IDAA, DTDAA and DGA are formed spontaneously as evinced by the negative values of ΔG. The overall changes in the values of ΔH and ΔS indicate that the complexes are both enthalphy and entropy stabilized. The negative values of ΔH ensure that the reactions are exothermic. The relatively smaller values of ΔH as compared to ΔS indicate that entropy is the principal driving force for the complex formation in aqueous solution, i.e. increase in randomness in the systems will increase the stability of complex because entropy is a solvent property.

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Ion-exchange Equilibria of Na^+-Ca^{2+}/Cl^- and Na^+-Mg^{2+}/Cl^- from Concentrated Solution

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The ion exchange of alkaline earth metal ions from their concentrated mixtures with alkali metal ions is studied. It is observed that as the concentrations of Ca^{2+} and Mg^{2+} in the solution increase, their uptake becomes smaller on the sodium form of Zeocarb-225. The no-selectivity line is reached when their concentrations reach 4.0 *N*.

THE behaviour of ions on exchange from concentrated solutions of Cu^{2+}/Na^+ on Dowex 50×8 was found by Subbarao and David[1] to be different from that from dilute solutions. They observed that the selectivity of ions by this exchanger decreases in concentrated solutions. However, the extent of such a decrease in selectivity is not known for alkali/alkaline earth metal ions by synthetic resins.

Bokil[2] found that when schoenite, K_2SO_4 ; $MgSO_4$; $6H_2O$, was added to soils with varying ion-exchange capacity e.g. red soil from Coimbatore, black soil from Bhavnagar and lateritic soil from Bangalore there was, in all cases, a reversal of uptake of Mg^{2+} beyond a certain concentration of schoenite and that K^+ was preferred by these clays. Hence we decided to inquire whether commercially available synthetic resins also show similar exchange behaviour in concentrated solutions.

We report here the results of our investigation on the behaviour of the strong acid exchanger, sodium form of zeokarb-225, from concentrated solutions of Na^+-Ca^{2+} and Na^+-Mg^{2+} as chlorides

Experimental

Na-form of zeokarb-225 resin was equilibrated with the solution mixtures (Na^+/M^{2+} ratios 1 : 9 to 9 : 1) of chlorides of $Na^+ + Ca^{2+}$ and $Na^+ + Mg^{2+}$ of different concentrations (1.0 *N* to 4.0 *N*).

After 24 hr, the concentration of divalent ion was estimated by EDTA titration[3] and fractions of metal ions in solutions and on the exchanger were calculated by difference. Results are given in Tables 1A and 1B. Equilibrium isotherms of Na^+-Ca^{2+} and Na^+-Mg^{2+} systems in three different concentrations (1 0, 2.0 and 4.0 *N*) were drawn by plotting equivalent ionic fractions of metal ions in

TABLE 1A—$Na^+ \rightleftharpoons Mg^{2+}(Cl^-)$ ION EXCHANGE EQUILIBRIA WITH ZEOKARB-225 AT 27±2°

(i) 25.0 ml 1.0 *N* mixture of 1 0 *N* NaCl+1.0 *N* $MgCl_2$ +1.0 g zeokarb-225 in Na^+ form.
(ii) 25.0 ml 2.0 *N* mixture of 2.0 *N* NaCl+2 0 *N* $MgCl_2$ +2.0 g zeokarb-225 in Na^+ form.
(iii) 25 0 ml 4.0 *N* mixture of 4.0 *N* NaCl+4.0 *N* $MgCl_2$ +4.0 g zeokorb-225 in Na^+ form.

Proportion of Na^+	Concentration of solns.	Fraction of Na^+ in solns.	Fraction of Na^+ on resin	Proportion of Na^+	Concentration of solns	Fraction of Mg^{2+} in solns	Fraction of Mg^{2+} on resin
Na_{10}		0.1995	0 088	Na_{10}		0.8005	0 9120
Na_{30}		0.3815	0.1754	Na_{30}		0.6185	0.8246
Na_{50}	1.0 *N*	0 5476	0.2608	Na_{50}	1 0 *N*	0.4524	0.7392
Na_{70}		0 7499	0.5069	Na_{70}		0.2500	0.4931
Na_{90}		0.9185	0.7730	Na_{90}		0.0815	0.2270
Na_{0}		0.1230	0 055	Na_{0}		0.8870	0.9450
Na_{10}		0.2268	0.1061	Na_{10}		0.7732	0.8939
Na_{30}		0.4137	0.2368	Na_{30}		0.5863	0.7614
Na_{50}	2.0 *N*	0.5923	0.4100	Na_{50}	2.0 *N*	0.4077	0.5900
Na_{70}		0.7398	0.5900	Na_{70}		0.2602	0.4100
Na_{90}		0.9101	0.8295	Na_{90}		0.0899	0.1705
Na_{0}		0.1279	0.0842	Na_{0}		0.8721	0.9158
Na_{10}		0.2103	0.2105	Na_{10}		0.7897	0.7895
Na_{30}		0.3869	0 4340	Na_{30}		0.6131	0.5660
Na_{50}	4.0 *N*	0.5608	0.5150	Na_{50}	4.0 *N*	0.4392	0.4850
Na_{70}		0.7464	0.7335	Na_{70}		0.2536	0.2665
Na_{90}		0.9114	0 9115	Na_{90}		0.0886	0.0885
Na_{0}		0 1205	0.1150	Na_{0}		0.8795	0.8850

Na_{10} means 10.0 ml of NaCl solution mixed with 90.0 ml of $MgCl_2/CaCl_2$. Similarly for Na_{20}, Na_{30}, etc.

TABLE 1B—$Na^{+} \rightleftharpoons Ca^{2+}(Cl^{-})$ ION EXCHANGE EQUILIBRIA WITH ZEOKARB-225.

(i) 25.0 ml 1 0 *N* mixture of 1.0 *N* NaCl + 1 0 *N* $CaCl_2$ + 1.0 g zeokarb-225 in Na^{+} form.
(ii) 25.0 ml 2.0 *N* mixture of 2.0 *N* NaCl + 2.0 *N* $CaCl_2$ + 1 0 g zeokarb-225 in Na^{+} form.
(iii) 25.0 ml 4 0 *N* mixture of 4.0 *N* NaCl + 4.0 *N* $CaCl_2$ + 4.0 g zeokarb-225 in Na^{+} form.

Proportion of Na^{+}	Concentration of solns.	Fraction of Na^{+} in solns.	Fraction of Na^{+} on resin	Proportion of Na^{+}	Concentration of solns	Fraction of Ca^{2+} in solns.	Fraction of Ca^{2+} on resin
Na_{10}		0.2066	0.0460	Na_{10}		0.7935	0.9540
Na_{30}		0.3689	0.1074	Na_{30}		0 6911	0 8926
Na_{50}	1.0 *N*	0.5622	0.2306	Na_{50}	1.0 *N*	0.4378	0.7694
Na_{70}		0.7308	0 4054	Na_{70}		0.2692	0.5946
Na_{90}		0 9095	0.6273	Na_{90}		0.0905	0.3727
Na_{0}		0.1163	0 0269	Na_{0}		0.8837	0.9731
Na_{10}		0 2193	0.1384	Na_{10}		0.7807	0.8616
Na_{30}		0.3995	0.2422	Na_{30}		0.6005	0.7578
Na_{50}	2.0 *N*	0.5920	0.4070	Na_{50}	2.0 *N*	0.4080	0.5930
Na_{70}		0 7381	0.5210	Na_{70}		0.2619	0.4790
Na_{90}		0.9102	0.8335	Na_{90}		0.0898	0.1665
Na_{0}		0.1309	0 0710	Na_{0}		0 8691	0.9290
Na_{10}		0.2103	0.2105	Na_{10}		0 7897	0 7895
Na_{30}		0 3869	0.3340	Na_{30}		0.6131	0.6660
Na_{50}	4.0 *N*	0.5608	0.5150	Na_{50}	4 0 *N*	0.4392	0.4850
Na_{70}		0.7464	0.7235	Na_{70}		0.2536	0 2765
Na_{90}		0.9166	0.8658	Na_{90}		0.0834	0.1842
Na_{0}		0.1176	0.0955	Na_{0}		0.8824	0.9045

solutions against equivalent ionic fractions of metal ions on exchanger and are shown in Figs. 1 and 2.
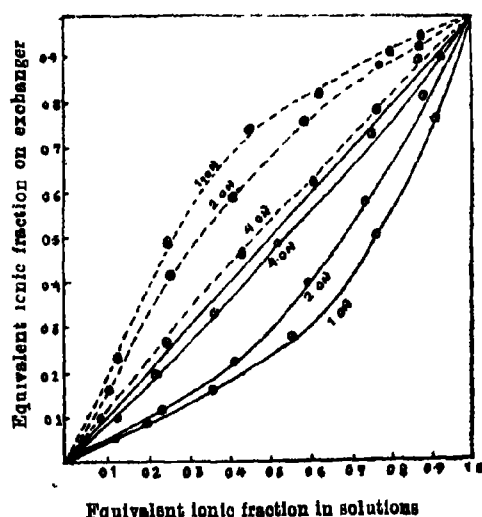
Fig. 1. $Na^{+} \rightleftharpoons Mg^{2+}$ (Cl') exchange isotherm for zeokarb-225 in Na^{+} form with 1.0, 2.0 and 4.0 *N* metal ion solutions at 27 ± 2°.

⊙ = Na^{+} ⊗ = Mg^{2+}

It can be seen from the results in Table 1A that fraction of Na^{+} on the resin from $MgCl_2$ solution is 0.055, 0.0842 and 0.1150 meq, respectively with the 1.0, 2.0 and 4.0 *N* metal ion concentrations. Similarly, corresponding fraction of Mg^{2+} on resin is 0.9455, 0.9158 and 0.8850 meq from 1.0, 2.0 and 4.0 *N* metal ion concentrations. The fraction of
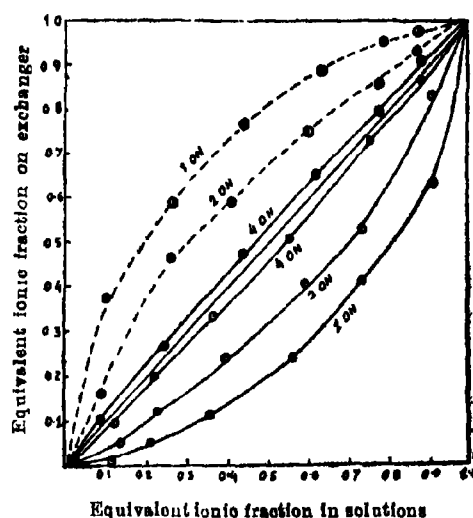
Fig. 2 $Na^{+} \rightleftharpoons Ca^{2+}$ (Cl') exchange isotherm for zeokarb-225 in Na^{+} form with 1 0, 2.0 and 4.0 *N* metal ion solutions at 27 ± 2°.

O = Na^{+} ⊗ = Ca^{2+}

Ca^{2+} on the exchanger is also found to decrease as 0.9731, 0.9290 and 0.9045 meq with the respective concentrations of solution of Mg^{2+}.

Thus, both Ca^{2+} and Mg^{2+} are exchanged on resins to a lesser extent from more concentrated solutions. The difference between the exchange of Mg^{2+} and Ca^{2+} on the resin is small, Ca^{2+} being exchanged to a slightly greater extent. Thus, a striking fact emerges that both Mg^{2+} and Ca^{2+} are exchanged less and less from concentrated solutions.

: can, therefore, be stated that a greater concentra-on of a bivalent ion results in lower exchange of ıat ion.

The decreasing exchange of bivalent metal ions y sodium form of zeokarb-225 from their increa-ngly more concentrated solutions can be explained n the following two grounds[4].

(1) *Donnan equilibrium :* The Donnan potential ıt up by a resin is directly proportional to the ınic molality in the resin and is inversely propor-onal to the solution concentration. Thus, with rge concentrations, the Donnan potential driving ıe counter ion into the resin is weaker. This sults in a lower exchange from concentrated ›lutions.

(2) *Ion-pair formation :* The concentrated solu-ons, dissociation of a salt into ions becomes naller. Ion-pairs are found to be present in an creasingly large amount as the concentration of ıe electrolyte increases[5]. The ion-pair formation greater in ions of larger valency. Hence, Mg^{2+} ıd Ca^{2+} ions form ion-pairs to a greater extent ıan alkali metals.

Equilibrium isotherms, which are shown in igs. 1 and 2 suggest that as the concentration of e solution increases, the uptake of bivalent metal ns on the Na^{+} form of the exchanger decreases. t about 4.0 *N* concentration of equilibrated solu-on, the equilibrium isotherms tend to coincide ith the line of zero-selectivity showing thereby at the exchanger has practically no preference for either the bivalent or the monovalent cations. Between Ca^{2+} and Mg^{2+}, Ca^{2+} is preferred to a slightly greater extent. This is because, as the concentration increases and the water activity falls, Ca^{2+} begins to gradually lose its hydration and tends to go into the resin phase and is found to be preferred[6] to Mg^{2+}. The effect, however, is very small as far as Ca^{2+} and Mg^{2+} are concerned.

It can be deduced from the above data obtained by batch experiments that in column operation, the conversion of the resin from the monovalent to the bivalent metal form (i.e. exhaustion cycle) can be achieved very well by employing dilute solutions of the bivalent metal ion concerned, whereas the regeneration cycle i.e. conversion of the exchanger from bivalent to monovalent form can be achieved by the use of concentrated solution of monovalent ions. Dilute solutions of such monovalent ions will also be more effective for the regeneration cycle.

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The Alkaline and Acid Hydrolysis of *n*-Butylacetate in Methanol-Water Mixtures

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Alkaline and acid hydrolysis of *n*-butylacetate was carried out in aqueous methanol at 10-25° for the alkaline and at 25-50° for the acid hydrolysis. In alkaline hydrolysis the reaction was irreversible and the bimolecular rate constants decreased steadily with progressive increase of the organic solvent in the reaction medium. In the acid hydrolysis, the reaction attained an equilibrium which depended upon the solvent composition. With progressive additions of methanol to the acidic ester solution, the *overall and reverse reaction rates increased gradually while the forward reaction rate* decreased. The characteristic kinetic behaviours are discussed in the light of the 'Back-Strain" effect and solvation phenomena. The effect of dielectric constant on reaction rate is interpretted by the treatment of Amis, based on simple electrostatic consideration of ion-dipole interactions. The isocomposition, isodielectric energy and logarithm of the Arrhenius frequency factor are also calculated and interpretted in terms of solvation effects. Mechanisms for alkaline and acidic hydrolyses are proposed which account for the role and the effects of the solvent on the reaction rate. *The thermodynamic parameters* ΔG^*, ΔH^*, ΔS^* *are calculated as a support to the proposed mechanisms.*

ALKALINE and acidic ester hydrolysis has been studied earlier[2,3]. Costeanu and Mateescu[4] studied the alkaline hydrolysis of *n*-butylacetate, propionate and butyrate in aqueous acetone. It was found that the rate of alkaline hydrolysis decreased with a decrease in the dielectric constant of the medium. Using acetone of mole fractions ranging from 0.124 to 0.377, the variation in the hydrolysis rate constant was found to follow the order $MeCO_2Bu > EtCO_2Bu > PrCO_2Bu$, i.e. it decreased with the decreasing dipole moment of the esters. The acid hydrolysis of butylacetate in different H_2O-acetone mixtures has been studied at 40, 50 and 60°[5]. The reaction rate constant was correlated with the dielectric constant and the viscosity of the mixed solvent. The values of the rate constants at every temperature passed through a minimum for a mole fraction of 0.4 of acetone. These data at different mole fractions of acetone permitted the calculation of the values of activation energy, frequency factor and thermodynamic parameters, which all show a maximum at the same mole fraction. The characteristic kinetic behaviours were discussed in the light of the solvation phenomena. In the present study, the alkaline and acidic hydrolysis of *n*-butylacetate in various methanol-water mixtures are investigated. The calculated thermodynamic data and other parameters are discussed as evidence supporting the proposed mechanism.

Experimental

Materials : *n*-Butylacetate (B. D. H.) was further purified by drying over sodium sulphate for 24 hr followed by fractional distillation. The fraction distilling at 124-125°/760 mm was collected and used. Methanol (E. Merck) was also purified as reported in literature[6]. Conductivity water was used for the different preparations and kinetic runs.

Preparation of solutions : An appropriate amount of the organic solvent was introduced in a measuring flask containing an weighed amount of *n*-butylacetate, affording a 0.05 *M* for the alkaline and 0.1 *M* for the acid hydrolysis. After attainment of thermal equilibrium the requisite quantity of NaOH solution, corresponding to 0.05 *M* for the alkaline hydrolysis, and that of HCl solution, corresponding to 0.1 *M* for the acid hydrolysis, was added to the ester solution. The volume was then made upto the mark and the flask placed in a thermostat at a temperature held constant within ±0.05°.

Rate determination : The rate of the alkaline hydrolysis was followed by withdrawing 5 ml samples of the reaction mixture. These were allowed to flow through an ion exchanger containing the cation Amberlite resin, IR-120 (H). The liberated acetic acid was determined by titration. The estimated infinity values in methanol-water mixtures indicated that the reaction is not of the reversible type. The values of the specific velocity constant k_2 were calculated using the second-order rate equation :

$$k_2 = \frac{x}{a(a-x)t} \qquad \dots (1)$$

where a is the initial concentration of both ester and alkali and x is the amount decomposed in

time t. In the acidic hydrolysis the reaction followed a first order law and was found to be of reversible nature. The rate constants were determined by titrating the liberated acetic acid with standard alkali. The effect of temperature on the position of equilibrium was investigated. No change in the equilibrium concentration was detected with change in temperature. So the infinity or equilibrium values were determined by heating the samples in sealed ampoules at 70° for 2-4 days until two successive values were identical. The rate constants k'_1 and k'_2 of the forward and backward reactions, respectively were calculated using the kinetic equation :

$$\frac{dx}{dt}=k'_1\ (a-x_e)-k'_2x_e \qquad (2)$$

The backward rate is assumed to obey a first order law, since the concentration of the acetic acid liberated by the forward reaction is small compared to the concentration of the total alcohol in the medium. Integration of equation (2) gives the expression,

$$(k'_1+k'_2)t=2.303\ \log x_e/(x_e-x) \qquad (3)$$

where x_e is the equilibrium value. It follows, therefore, from equation (3) that the plot of log $x_e/(x_e-x)$ versus t should give a straight line with a positive slope which is equal to $(k'_1+k'_2)/2.303$, and that :

$$k'_1=(k'_1+k'_2).x_e/a \qquad (4)$$

where a is the infinity value for the complete reaction.

Results and Discussion

1. *Effect of temperature :* Interpolated values of k_2 (in l. mole^{-1} sec^{-1}) for the alkaline hydrolysis of *n*-butylacetatate in presence of methanol-water mixtures in the temperature range 10-25° are given in Table 1, while the corresponding values

TABLE 1—INTERPOLATED VALUES OF K_2 (in l mole^{-1}sec^{-1}) FOR THE ALKALINE HYDROLYSIS OF *n*-BUTYLACETATE IN PRESENCE OF METHANOL-WATER MIXTURES

Wt. % of Solvent	10^2K_2 10°	15°	20°	25°
15	4.420	6.300	8.675	11.500
20	3.625	5.125	7.000	9.650
25	2.925	4.100	5.750	7.875
30	2.350	3.350	4.650	6 500
35	1.800	2.650	3.650	5.100
40	1.375	2.050	2.925	3.975
45	1.025	1.575	2.225	3.050
50	0.750	1.200	1 720	2.800
55	0 575	0.900	1.340	1.800
60	0 420	0.650	1 000	1.325
65	0.300	0.500	0.750	0.950
70	0.225	0.400	0.560	0.700
75	0.175	0 325	0.450	0.525
80	0 140	0.250	0.350	0.400

for the overall, forward and backward reactions, (k_{obs}, k'_1 and k'_2) respectively, for the acid hydrolysis are recorded in Table 2. Arrhenius equation is strictly obeyed. Good straight lines are obtained on plotting log k_2 versus 1/T, for alkaline hydrolysis as shown in Fig. 1. The values of the isocomposition activation energy, E_c, and frequency factor log A were calculated by the least square method and are compliled in Table 3. For the acid hydrolysis, good straight lines were obtained on plotting the log k' versus 1/T. The values of the forward E_{1c}, backward E_{2c}, observed $E_{c\ obs}$ activation energies, and the frequency factor log A for the forward reaction are also calculated by the least square method and recorded in Table 3. However, to obtain a more precise treatment of the results, the temperature dependence of the dielectric constant should be eliminated. This is achieved by calculating the isodielectric activation energies, E_d, from the corresponding rate constants in isodielectric solutions. The values of E_d for alkaline hydrolysis and the values of E_{1d}, E_{2d} and $E_{d\ obs}$ for the acid hydrolysis are given in Table 4.

TABLE 2—INTERPOLATED VALUES OF RATE CONSTANTS ($k\times10^6$ sec^{-1}) FOR THE ACID HYDROLYSIS OF *n*-BUTYLACETATE IN PRESENCE OF METHANOL-WATER MIXTURES

Wt % Solvent	25° 10^6k_{obs}	25° $10^6k'_1$	25° $10^6k'_2$	30° 10^6k_{obs}	30° $10^6k'_1$	30° $10^6k'_2$	40° 10^6k_{obs}	40° $10^6k'_1$	40° $10^6k'_2$	50° 10^6k_{obs}	50° $10^6k'_1$	50° $10^6k'_2$
15	1.700	0.900	0.800	2 850	1.680	1.170	6 800	3.740	3.060	14.000	7 220	6.780
20	1.800	0 815	0 985	3 000	1 560	1 440	6 900	3 380	3 520	14.400	6 920	7.480
25	1.875	0 760	1.115	3.200	1 415	1.785	7 000	3 090	3 920	15 000	6 580	8.420
30	1.900	0.705	1.195	3.350	1 290	2.060	7.100	2 850	4 250	15 800	6.270	9.530
35	2.050	0 655	1.395	3.550	1.170	2.380	7.300	2.650	4.650	17.300	5 980	11.320
40	2.175	0.610	1.565	3.750	1.067	2 683	7.650	2.500	5.150	18 600	5.690	12.910
45	2.350	0 575	1.775	4.000	0 990	3.010	8 050	2.370	5 680	20.600	5.420	15.180
50	2.550	0 547	2.003	4 250	0.925	3.325	8.700	2.280	6.420	22.900	5.180	17.720
55	2 740	0.523	2 217	4 600	0.875	3 725	9.500	2.200	7.300	25 800	4.960	20.940
60	3 000	0.505	2 495	4.950	0 835	4.115	10 600	2 240	8.460	29 200	4 750	24 450
65	3.400	0.493	2 907	5.150	0.800	4.650	13.000	2.080	10.920	33 600	4.570	29.030
70	3.875	0.487	3 388	6.200	0.775	5 425	13 600	2.040	11 560	39.000	4.430	34.570
75	4 650	0.482	4.168	7.200	0.765	6 435	15.800	2 000	13.800	46 000	4.340	41.660
80	5.725	0.475	5.250	8.550	0.760	7.790	19.600	1.980	17.620	55 800	4.275	51.525
85	7.275	0.473	6.802	10.650	0.755	9 895	25.400	1 960	23.440	69 000	4.240	64.760
90	9.250	0.470	8.780	13.750	0.750	13 000	33.800	1.950	31.850	83.400	4.200	79.200

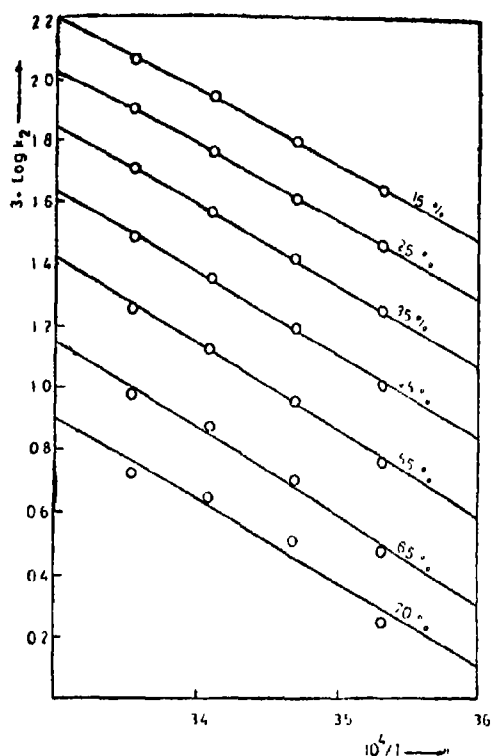



Fig. 1. Determination of activation energy in methanol-water mixtures.

TABLE 3—ISOCOMPOSITION ENERGIES OF ACTIVATION (in Kcal $mole^{-1}$) AND FREQUENCY FACTORS IN METHANOL-WATER MIXTURES

Wt % solvent	Alkaline hydrolysis		Acid hydrolysis			
	E_c	log A	E_{1c}	E_{2c}	$E_{c\ obs}$	log A
15	10 69	9.90	15 67	19.34	16.12	12.48
20	10.89	9 96	15.99	15 75	15 84	12.67
25	11 09	10.03	16.16	15 38	15.71	12.75
30	11 29	10 08	16 40	15 55	15 88	12.90
35	11 55	10.17	16 67	15 58	15.90	13 05
40	11 87	10 31	16.91	15 65	16 02	13.20
45	12 13	10.39	17.05	15 87	16.18	13 27
50	12 19	10.53	17.16	16 18	16.41	13.33
55	12 81	10.67	17.23	16.66	16.75	13 36
60	13 01	10.68	17.22	17.04	17.08	13.33
65	12.98	10 52	17.17	17.49	17.45	13 28
70	12.58	10.10	17.08	17.43	17.40	13.21
75	12.20	9.71	17.00	17.34	17.31	13.14
80	11.70	9.22	16.98	17.22	17.30	13 13
85	—	—	16.95	17.17	17 26	13.10
90	—	—	16.93	16.95	16.95	13.08

TABLE 4—ISODIELECTRIC ACTIVATION ENERGIES (in Kcal $mole^{-1}$) FOR METHANOL-WATER MIXTURES

D	Alkaline hydrolysis	Acid hydrolysis		
	E_d	E_{1d}	E_{2d}	$E_{d\ obs.}$
40	—	17.34	9.19	13.86
50	18.54	17.79	12.91	14.40
55	18.23	—	—	—
60	17.61	18.00	12.98	14.40
65	17.25	—	—	—
70	16.59	13.37	13 37	14.29

Both of velocity constants in the alkaline hydrolysis and the forward reaction for the acid hydrolysis are found to decrease with the progressive addition of methanol. This trend is ascribed to the decrease of water concentration as well as to the lowering of the dielectric constant of the medium. On the other hand, the isocomposition activation energy, E_c, increases to a maximum value for both alkaline and acidic hydrolysis, while isodielectric activation energies, E_d, increase with the decrease of the dielectric constant in alkaline hydrolysis and pass through maximum in case of acid hydrolysis. This may be due to the solvation of the activated complex to a less extent than that of the reactants. Although the changes in log A are generally more sensitive to solvent composition, the variation of the activation energy with solvent composition is more pronounced than that of log A[7].

Thermodynamic data of the activated complex : The effect of changes in solvent composition on the rate constant of the reaction is conveniently verified in terms of the thermodynamic parameters of activation. These are calculated at different temperatures for different solvent composition in both alkaline and acidic hydrolysis and are compiled in Tables 5 and 6.

In both alkaline and acidic hydrolysis, the data of ΔG^* indicate that solvation of the reactants is more than that of the activated complex which is in agreement with the decrease of the bimolecular rate constant in alkaline hydrolysis and the forward rate constant in acidic hydrolysis as the concentration of the methanol in the mixture increases. The heat content change ΔH^*, shows a maximum in both alkaline and acidic hydrolysis. This may be a direct consequence of the behaviour of the isocomposition activation energy with the increasing organic solvent content. The non-linear relation between ΔS^* and the solvent composition in alkaline and acidic media indicate specific solvation and hence a non-random distribution of the solvent molecules[8].

Effect of dielectric constant : Akerlof's data[9] are used to obtain the dielectric constant values for the mixtures under investigation by interpolation. For the alkaline hydrolysis, the plots of log k_2 against 1/D (Fig 2) give straight lines with negative slopes. Deviation from this linearity are observed at high solvent concentration (region of low dielectric constant). These deviations are probably due to the preferential solvation of the activated complex by water, the higher dielectric constant component. Consequently the distribution of the solvent molecules will be less random, and the values of D in the immediate vicinity of the ion will diverge considerably from that in the bulk, which is the value measured experimentally. This effect becomes larger as the dielectric constant becomes lower. In the acidic hydrolysis, an increase of the dielectric constant of the mixtures is found to lead to an increase in the rate of the forward reaction. However, the rate of the overall and reverse

TABLE 5—THERMODYNAMIC DATA IN METHANOL-WATER MIXTURES ΔG* AND ΔH* IN KCAL/MOLE, ΔS* IN CAL/MOLE/DEGREE

	Wt % Solvent	15	20	25	30	35	40	45	50	55	60	65	70	75	80
	ΔG*	18.300	18.412	18.532	18.655	18.805	18.957	19.122	19.298	19.448	19.624	19.814	19.976	20.117	20.243
10°	ΔH*	10.130	10.325	10.529	10.725	10.985	11.308	11.570	11.929	12.261	12.449	12.418	12.021	11.686	11.137
	−ΔS*	28.854	28.561	28.264	28.006	27.618	27.014	26.671	26.025	25.382	25.340	26.120	28.095	29.952	32.160
	ΔG*	18.430	18.548	18.676	18.792	18.926	19.073	19.224	19.380	19.545	19.731	19.881	20.009	20.128	20.278
15°	ΔH*	10.120	10.315	10.519	10.715	10.975	11.298	11.560	11.919	12.251	12.439	12.408	12.011	11.626	11.127
	−ΔS*	28.839	28.572	28.308	28.031	27.599	26.982	26.597	25.893	25.313	25.306	25.984	27.756	29.505	31.758
	ΔG*	18.574	18.699	18.814	18.944	19.079	19.208	19.367	19.517	19.662	19.823	20.001	20.171	20.298	20.445
20°	ΔH*	10.110	10.305	10.509	10.906	10.965	11.289	11.550	11.909	12.241	12.429	12.398	12.001	11.616	11.117
	−ΔS*	28.873	28.694	28.330	28.101	27.679	27.018	26.666	25.953	25.315	25.223	25.936	27.870	29.616	31.820
	ΔG*	18.733	18.837	18.958	19.071	19.215	19.363	19.520	19.687	19.832	20.014	20.211	20.392	20.562	20.723
25°	ΔH*	10.100	10.295	10.499	10.696	10.955	11.279	11.540	11.899	12.231	12.419	12.388	11.991	11.606	11.107
	−ΔS*	28.955	28.650	28.372	28.090	27.704	27.114	26.765	26.121	25.494	25.474	26.238	28.177	30.039	32.252

TABLE 6—THERMODYNAMIC DATA IN METHANOL-WATER MIXTURE ΔG* AND ΔH* IN KCAL/MOLE, ΔS* IN CAL/MOLE/DEGREE

	Wt % Solvent	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
	ΔG*	24.339	24.397	24.439	24.489	24.527	24.569	24.604	24.634	24.660	24.681	24.695	24.703	24.709	24.717	24.720	24.724
25°	ΔH*	15.079	15.393	15.670	15.810	16.073	16.318	16.464	16.568	16.633	16.628	16.576	16.490	16.407	16.387	16.362	16.335
	−ΔS*	31.057	30.200	29.745	29.091	28.355	27.674	27.335	27.058	26.925	27.012	27.231	27.544	27.843	27.940	28.085	28.137
	ΔG*	24.381	24.425	14.184	24.540	24.599	21.654	24.699	24.740	24.774	24.802	24.828	24.847	24.855	24.859	24.863	24.867
30°	ΔH*	15.069	15.383	15.660	15.800	16.063	16.308	16.444	16.558	16.623	16.618	16.566	16.480	16.397	16.377	16.352	16.325
	−ΔS*	30.717	29.828	29.438	28.831	28.157	27.532	27.232	26.991	26.868	26.998	27.252	27.599	27.898	27.978	28.075	28.177
	ΔG*	24.707	21.770	24.828	24.876	24.922	21.958	24.991	25.015	25.037	25.055	25.072	25.084	25.097	25.103	25.109	25.113
40°	ΔH*	15.049	15.363	15.540	15.780	16.043	16.288	16.424	16.598	16.603	16.598	15.547	16.461	16.377	16.357	16.332	16.305
	−ΔS*	30.841	30.039	29.658	29.048	28.852	27.686	27.357	27.070	26.935	27.006	27.226	27.539	27.844	27.928	28.089	28.126
	ΔG*	25.094	25.121	25.151	25.185	25.215	25.247	25.278	25.307	25.335	25.363	25.388	25.408	25.421	25.431	25.436	25.442
50°	ΔH*	15.029	15.344	15.521	15.760	16.023	16.268	16.401	16.518	16.583	16.578	16.527	16.441	16.358	16.337	16.312	16.285
	−ΔS*	31.145	30.258	29.810	29.164	28.444	27.785	27.460	27.198	27.081	27.186	27.421	27.749	28.047	28.139	28.234	28.337

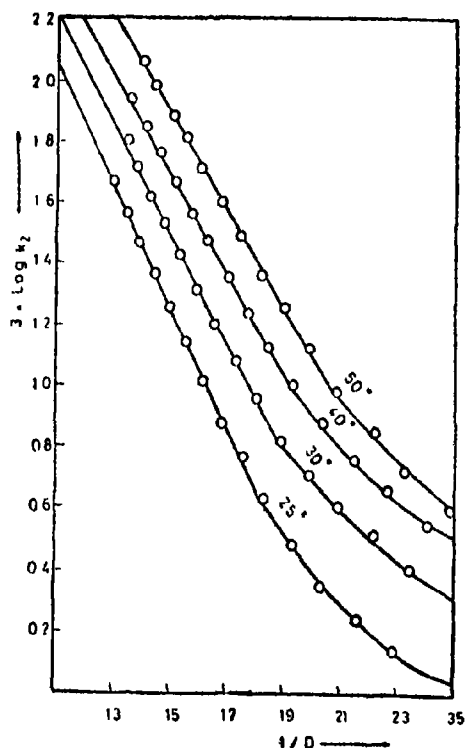



Fig. 2. Variation of k with dielectric constant in methanol-water mixtures.

reactions decrease with increasing dielectric constant. Plots of log k'_1 against 1/D give straight lines with negative slopes in the high dielectric range, but deviations from linearity become evident as the dielectric constant decreases. This deviation is probably due to the preferential solvation of the activated complex by water.

Effect of solvent composition : In the alkaline hydrolysis, the rate constants are found to decrease with the decrease of water concentration in the medium. The plots of log k_2 versus log C_W give straight lines having a positive slope in water-rich mixtures, followed by a curvature in the regions of solvent-rich mixtures (Fig. 3). The slopes obtained are found to vary slightly with temperature, and have a mean value of 3.15 in the water-rich mixtures. These slopes represent the number of water molecules involved in the formation of the activated complex.

The variation of the rate constant as a function of the concentration of alcohol in the solvent mixture is attributed to many factors[10,11], concerning the nucleophile and the substrate. It has been reported that when sodium hydroxide is dissolved in ethanol (or methanol) the solution would mainly contain ethoxide (or methoxide) rather than hydroxide ions[12-14] and many pazzling facts have been explained in the light of this assumption[15,16].

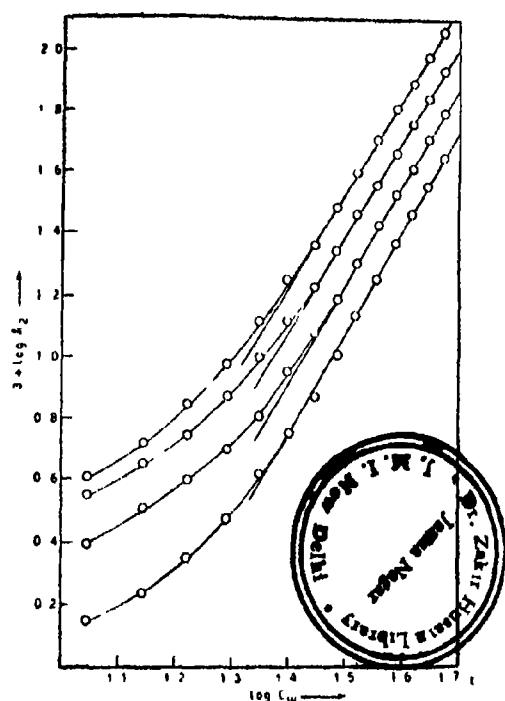
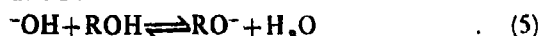



Fig. 8. Variation of k_2 with water concentration in methanol-water mixtures

The *extensive investigations* done by Brown *et al*[17] on the steric effects on equilibria were extended to the study of "back strain" effects on the basicity of alkoxide[18]. It was concluded that the basicity of methoxide ion is less than that of hydroxide ions. Since the rate of the reaction is dependent on the stoichiometric concentration of the base anion, it is expected that the rate will decrease due to the decrease in the stoichiometric concentration of the hydroxide ion by the addition of the organic solvent component, according to the equation :

$$^{-}OH + ROH \rightleftharpoons RO^{-} + H_2O \quad (5)$$

Thus, it would not be surprising in this case that the rate constant decreases continuously by the successive addition of methanol to the reaction medium although the dielectric constant of the medium decreases.

In the acidic hydrolysis, the overall and reverse rate constants are found to increase as the water concentration in reaction medium decreases. However, the forward rate is found to decrease with decreasing water concentration. The plot of log k'_1 against log C_W gives straight lines of mean value unit slope. These slopes represent the number of water molecules involved in the formation of the activated complex. The lines are straight in the range of high concentration of water but deviations from linearity become evident as the water concentration decreases.

It is clear that the decrease of the forward rate constant with the progressive addition of alcohol is harmonic with the decrease of water concentration and the decrease of the dielectric constant of the medium, also the decrease of acidity of hydrochloric acid (the increase of basicity of water) accompanying the addition of alcohol. This has been attributed[19] to the progressive breakdown of the tetrahedral structure of water. Thus, instead of having the structure $(H_2O)_4H^+$ one may have the species $(H_2O)_3H^+$ besides, since the proton affinity in the open structure $(H_2O)_4H^+$ is less than that in the compact structure, the latter will be holding the proton more firmly and hence in the presence of alcohol, water will be more basic, and thus the net result is a decrease in rate.

Proposed mechanism : In the alkaline hydrolysis, the change in the relative concentrations of the hydroxide and alkoxide ions due to the change in the solvent composition is accommodated by the equilibrium represented by equation (5). Accordingly, the overall reaction rate may be represented by equation (6);

$$\text{Rate} = k_2 \,[\text{Ester}]\,[\text{Base}] \quad (6)$$

where $[\text{Base}] = [\bar{O}H] + [R\bar{O}]$ ... (7)

accordingly, equation (6) becomes,

$$\text{Rate} = [\text{Ester}]\,\{k'\,[\bar{O}H] + k''\,[R\bar{O}]\} \quad ... (8)$$

Substituting for OH in equation (8) from equilibrium (5) and rearranging, we obtain,

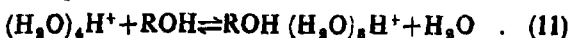
$$\text{Rate} = [\text{Ester}]\,[RO]\left\{\frac{k'}{K}\frac{[H_2O]}{[ROH]} + k''\right\} \quad ... (9)$$

therefore,

$$k_{obs} = \frac{k'}{K}\frac{[H_2O]}{[ROH]} + k' \quad (10)$$

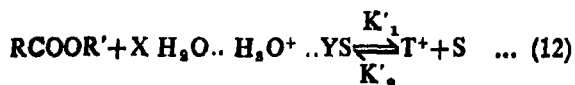
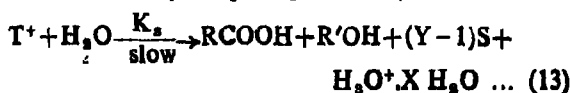
where k' and k'' are the specific rate constants for the reaction catalysed by OH and RO ions, respectively and K is the equilibrium constant represented by equation (5). The increase of methanol content will cause a decrease in the first term of the right hand side of equation (10) as well as in k'' due to the increase in RO concentration according to equation (5) and hence k_{obs} will also decrease.

In acidic hydrolysis the forward rate of reaction decreases with increase in the methanol concentration. It is known that[19] the proton is hydrated by four water molecules and it has the structure $(H_2O)_4H^+$ in the cluster shape. In mixed solvents, the net reaction actually taking place is the substitution of water by alcohol in the cluster, for example :

$$(H_2O)_4H^+ + ROH \rightleftharpoons ROH\,(H_2O)_3H^+ + H_2O \quad (11)$$

Hence, the following reactions mechanism is proposed.

$$RCOOR' + X\,H_2O..\,H_3O^+\,..YS \underset{K'_2}{\overset{K'_1}{\rightleftharpoons}} T^+ + S \quad ... (12)$$

(Fast pre-equilibrium)

$$T^+ + H_2O \xrightarrow[\text{slow}]{K_3} RCOOH + R'OH + (Y-1)S + H_3O^+.X\,H_2O \quad ... (13)$$

where S is a solvent molecule and T^+ stands for the solvated transition state in which the solvation is maintained through H-bonding.

Assuming a steady state approximation,

$$K'_1 [Ester][H_3O^+] = K'_2[T][S] + K_3[T][H_2O] = [T]\{K'_2[S] + K_3[H_2O]\} \quad (14)$$

$$[T] = \frac{K'_1[Ester][H_3O^+]}{K'_2[S] + K_3[H_2O]} \quad (15)$$

The rate of reaction is given by

$$= K_3[T][H_2O] \quad (16)$$

$$= \frac{K_3K'_1[Ester][H_3O^+][H_2O]}{K'_2[S] + K_3[H_2O]} \quad (17)$$

$$= \frac{K_3K'_1[Ester][H_3O^+]}{K'_2\frac{[S]}{[H_2O]} + K_3} \quad (18)$$

since K_3 is small in comparison to K'_2 thus the

$$rate = \frac{K'_1K_3}{K'_2}\frac{[Ester][H_3O^+][H_2O]}{[S]} \quad (19)$$

This mechanism verifies the direct dependence of the rate on the water concentration and the inverse proportionality of the rate with the organic solvent concentration.

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Thermal Degradation of *p*-Anisic Acid-Formaldehyde Condensation Product

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p-Anisic acid has been condensed with formaldehyde and the thermal properties of the resin obtained have been studied by differential thermal analysis (DTA), and thermogravimetry (TG). Kinetics parameters for the decomposition reaction have been determined by different methods.

A survey of literature[1-4] reveals that products resulting from the condensation of benzoic acid and substituted benzoic acid with formaldehyde are industrially important. The present paper describes an attempt to study the thermal behaviour of such a condensation product using thermogravimetry (TG) and differential thermal analysis (DTA) techniques.

Experimental

Preparation of p-*anisic acid-formaldehyde condensation product :* *p* Anisic acid (15.2 g), paraformaldehyde (3.0 g), glacial acetic acid (50 ml) and conc. sulfuric acid (1.0 ml) were mixed and heated at 120° for 2 hr. The reaction mixture was poured into cold distilled water. The solid was dried in vacuum at room temperature.

The Linsesis thermo-balance for thermogravimetry and a micro cell[5] for differential thermal analysis were used for the kinetics of decomposition using 25 or 50 mg of the resin for TG and 3 mg of the resin mixed with aluminium oxide for DTA studies at different heating rates in static air.

Results and Discussion

The condensation product did not soften at 240°. It started to decompose at higher temperature. The kinetics parameters were obtained using Chatterjee[6] (Table 1a), Anderson-Freeman[7], Broido[8] and Flynn and Wall[9] methods from the TG-study (Table 1b) and using Reich[10] and Kissinger[11] method from DTA (Table 2). When the samples were heated at different rates (R.H.) for the TG study, the degradation occurred in two stages (Fig. 1). Major decomposition (60%) took place in the second step. The decomposition started at ~245° and ended at ~600°. The activation energy, E_A, obtained from the TG-study using the Chatterjee method for the first and the second stage of decomposition respectively ranged from ~15 to ~26 Kcal mol^{-1}. The decomposition followed a first order kinetics for both steps. The starting temperature of decomposition increased with increasing heating rate (Table 1a). The Anderson-Freeman method gave an E_A in the range of ~22 to ~32 Kcal mol^{-1}.

TABLE 1a—KINETICS PARAMETERS (TG)

R.H. (°C min^{-1})	Amount mg	Decomposition temp. °C	ΔT °C	Weight loss %	Chatterjee method E_A (Kcal mol^{-1})	Chatterjee method Order of reaction n
1.0	50	245-300		40	20 0	0.8
		300-570	325	60	25.5	1.1
	25	245-300		40	19.5	0.8
		300-570	325	60	25.0	1.1
2 5	50	260-320		40	18.0	1.0
		320-580	320	60	24.8	1.1
	25	260-320		40	18.8	1 0
		320-580	320	60	25.0	1.1
4 0	50	270-335		40	16.5	0.9
		335-590	320	60	24.0	1.0
	25	270-335		40	16.8	0 9
		335-590	320	60	23.5	1.0
6.5	50	290-340		40	15.0	1.3
		340-600	310	60	20.2	1.1
	25	290-340		40	15.8	1.3
		340-600	310	60	20.5	1.1

TABLE 1b—KINETICS PARAMETERS (TG)

R.H. (°C min^{-1})	Amount mg	Energy of activation E_A (Kcal mol^{-1})			Order of reaction n	
		Broido method	Flynn-Wall method	Anderson-Freeman method	Broido method	Anderson-Freeman method
1.0	50	18.1	33.1	29.5	1.0	0.8
	25	18.9	27.5	31.5	1.0	0 8
2.5	50	15.5		26.3	1 0	0.9
	25	15.9		27.8	1.0	1.0
4.0	50	14 8		25.1	1.0	0.9
	25	14.3		25.5	1.0	1.1
6 5	50	12.9		21 8	1.0	0.8
	25	13.5		22.6	1.0	1.3

TABLE 2—KINETICS PARAMETERS (DTA)

R.H. (°C min^{-1})	Peak temperature (°C)	Energy of activation, E_A (Kcal mol^{-1})		Order of reaction n	
		Reich method	Kissinger method	Reich method	Kissinger method
1.0	480	43.0	37.8	1.3	0.8
2.5	490	38.1		1.2	0.9
4.0	495	35.5		1.0	1.1
6.5	505	30.1		1.2	0.9

Fig. 1. TG

Fig. 2 DTA

TG and DTA curves of p-anisic-formaldehyde condensate product at various heating rate (R.H.).
1—6.5°/min 2—4.0°/min
3—0.5°/min 4—1 0°/min

That obtained from the Broido method varied from ~13 to ~19 Kcal mole⁻¹. The Flynn and Wall method gave a slightly higher E_A value compared to the other methods. In general, the decomposition followed first order kinetics.

The thermal parameters resulting from the DTA study using the method of Reich and Kissinger are given in Table 2. The degradation is exothermic (Fig. 2). The temperature for the peak maxima varied from ~480 to ~505° for different R. H. *The activation energy obtained employing the Reich method varied from ~30 to ~43 Kcal mol⁻¹* with the decreasing R.H. The Kissinger method *yielded an E_A value of ~38 Kcal mole⁻¹. This value represents the overall degradation process.* The evaluation of the data by this method involves many thermograms at different heating rates and assumes E_A to be the same for the degradation of the sample.

The E_A values from the DTA study are higher in comparison to those obtained from TG study. This could be ascribed to the retardation of decomposition of the polymer sample, which is sandwiched between neutral media in a narrow cavity of the DTA-micro cell, compared to the decomposition in a shallow boat of the TG sample holder.

The values of activation energy resulting from different methods are different, indicating that they depend on the heating rate and the method of calculation ; different methods involving different limitations.

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Thermal Decomposition of Irradiated Strontium Nitrate

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The influence of γ-irradiation on the kinetics of thermal decomposition of strontium nitrate has been studied over the temperature range 580-625°. Decomposition occurs in the molten state in four stages, viz., (i) initial gas evolution, (ii) induction, (iii) acceleratory and (iv) decay. The kinetics of stages (i) and (ii) could not be studied with any degree of certainty. The acceleratory and decay stages analyse according to the Prout-Tompkins relationship. Activation energies for these two stages calculated from the Prout-Tompkins constants are 102.9 and 26.3 kcal mole^{-1}, respectively. Irradiation increases initial gas evolution and shortens the induction period. It also enhances the rate constants in the acceleratory and decay stages. The activation energy for the acceleratory stage is diminished while that for the decay stage is increased.

THE role of irradiation in the thermal decomposition of inorganic salts has been studied and it has been observed that preirradiation with energetic radiations shortens the period of induction, if any, and enhances the rate constants for both the acceleratory and the decay stages[1-3]. Production of chemical damage, displacements and extended lattice defects are the predominant effects of irradiation on systems containing molecular ions[4-6]. The influences of irradiation on solid decomposition are therefore ascribed to these effects which provide as well as facilitate formation and growth of nucleation centres[7]. In the earlier work[1,2] the relative contribution of crystal defects and chemical damage fragments was not ascertained. It was therefore of interest to irradiate a substance in the solid state generating both crystal defects and chemical damage and to subsequently follow its decomposition in the molten condition when the crystal defects no longer exist but the chemical damage persists. Strontium nitrate has been chosen for this study because the substance decomposes at temperatures well above the melting point and moreover because the kinetics of thermal annealing of irradiation damage in the substance below its melting point has been studied in detail recently[8,9].

Experimental

Material : AR grade strontium nitrate was used in the form of fine powder. It was dried *in vacuo* over phosphorus pentoxide.

Irradiation : Samples sealed in glass ampoules were irradiated with ^{60}Co γ-rays to different doses between 100 and 400 Mrad at the dose rate of 0.2 Mrad hr^{-1}. The irradiated samples were also preserved over phosphorus pentoxide before thermal decomposition studies.

Decomposition apparatus and procedure : The decomposition apparatus and procedure employed were the same as those reported earlier[1]. Fluorolube HO oil was used as manometric liquid and Kel-F grease as lubricant for stopcocks. In making a run, about 50 mg of strontium nitrate, accurately weighed, was decomposed in a thermostatically controlled electric furnace at temperature in the range 580-625° (±0.5°) and the pressure, p, of the evolved gases developed at different time intervals was measured at each temperature with a cathetometer. The final pressure P_f was obtained by heating at 800 till there was no further pressure rise and then cooling to the respective temperature of each run. The data have all been normalized to a mass of 50 mg. From the pressure values the fractional decomposition $\alpha = p/p_f$ was computed.

Estimation of damage : The nitrite produced by irradiation was estimated spectrophotometrically[8].

Isothermal annealing : Irradiated crystals were annealed in air isothermally at 300 ± 1° in a thermostatic electric hot air oven for different time intervals and the extent of annealing determined. The thermal decomposition behaviour of the partially preannealed samples was studied at 600°.

Results and Discussion

Data for the dependence of fractional decomposition, α, for unirradiated strontium nitrate on the heating time, t, at different temperatures in the range 580-625° are contained in Fig. 1. The curves are sigmoid in nature, as are characteristic of autocatalytic type reactions, the decomposition proceeding mainly through four stages, viz., (i) initial rapid gas evolution corresponding to $\alpha = 0$, (ii) an

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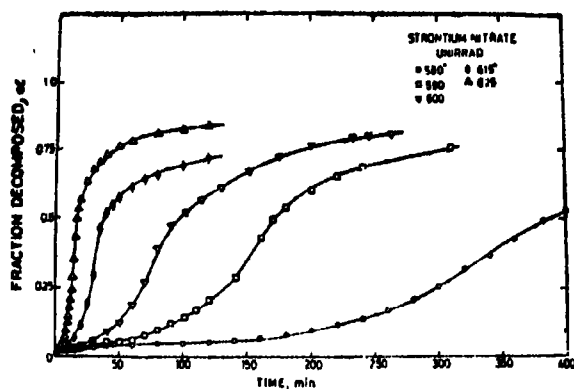


Fig. 1. Thermal decomposition of unirradiated strontium nitrate at different temperature.

induction period followed by (iii) acceleratory and (iv) decay stages, respectively.

The initial evolution of gas was extremely rapid and was complete in the first min of heating. It was not possible therefore to determine the kinetics and activation energy of the process. Although the initial reaction in solid decomposition can be ascribed to either physical desorption or to true surface decomposition depending on the activation energy of the process, in decompositions occurring in the molten state, as in the present case, it would only be due to release of occluded air.

The kinetics operating in the induction period also could not be determined with any reasonable degree of certainty. The induction period itself decreases markedly with rise in temperature (Fig. 1).

The α-t curves have been analysed according to the Prout-Tompkins relationship[10] (Fig 2)

$$\log [\alpha/(1-\alpha)] = k_{1,2}\, t + c$$

k has two values corresponding to the acceleratory and the decay stages of the reaction. The Arrhenius

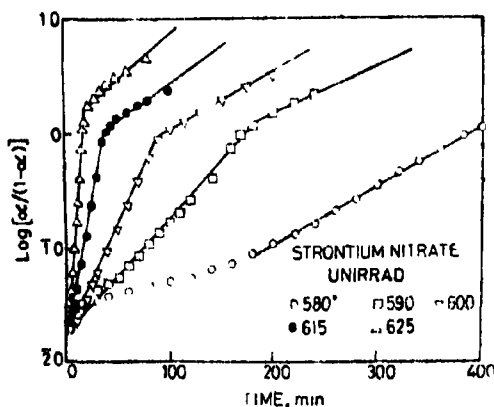



Fig. 2. Prout-Tompkins analysis of the kinetics of thermal decomposition of unirradiated strontium nitrate.

plots for the Prout-Tompkins constants k_1 and k_2 are linear and yield activation energies E_1 and E_2 of 102.9 and 26.3 kcal for the acceleratory and the decay stages, respectively (Table 1).

Table 1—Activation Energies for the Decomposition of Strontium Nitrate (kcal mole^{-1})

Sample	E_1	E_2
Unirradiated	102.9	26 8
100 Mrad	100.1	30.9
400 Mrad	88.9	39.1

The relation between the measure of the chemical damage[8] in terms of %NO_2^- induced in strontium nitrate in the present experiments and the dose of γ-irradiation is given in Fig. 3. The chemical damage induced is susceptible to thermal recovery. The fraction annealed[8] at 300° during different time intervals from 0-100 hr in the case of strontium nitrate irradiated to 400 Mrad ^{60}Co γ-rays are also shown in Fig. 3.

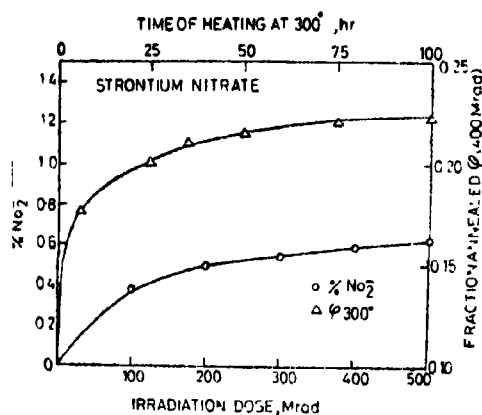



Fig. 3. The dependence of chemical damage in strontium nitrate on the irradiation dose and the time dependence of annealing

Comparison of the α-t characteristics at 600° for the decomposition of strontium nitrate irradiated to 100, 200, 300 and 400 Mrad ^{60}Co γ-rays with those for the unirradiated material (Fig. 4) shows that pronounced changes are brought about in the

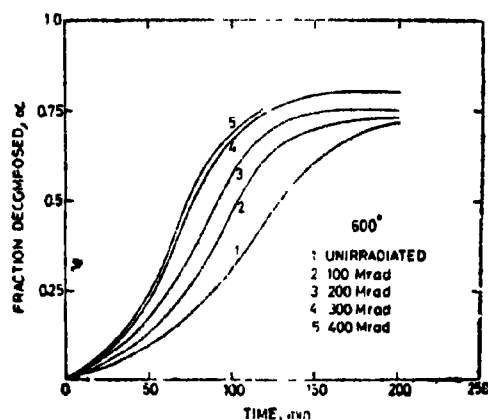



Fig. 4. Effect of γ-irradiation dose on the thermal decomposition of strontium nitrate at 600°.

nature of the decomposition by irradiation, particularly at the higher γ-ray doses employed. The induction period is shortened and is virtually absent in the material irradiated to 400 Mrad.

Data for the decomposition of strontium nitrate irradiated to 100 and 400 Mrad over a temperature range 580-625° presented in Figs. 5 and 6 are best fitted by the Prout-Tompkins relationship. The activation energies E_1 and E_2 for the Prout-Tompkins constants are given in Table 1. The results,

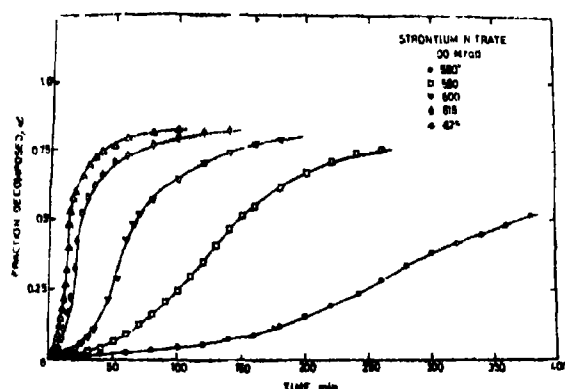



Fig 5 Thermal decomposition of 100 Mrad γ-irradiated strontium nitrate at different temperatures

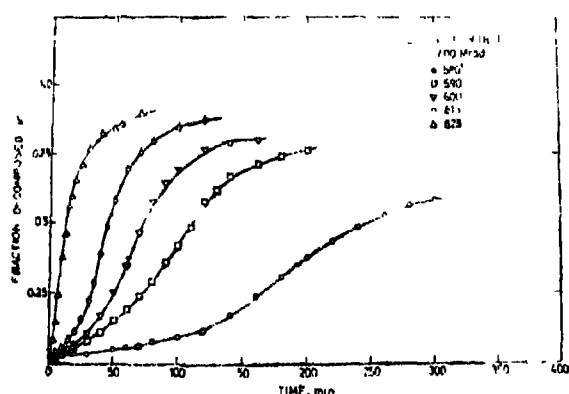



Fig 6 Thermal decompositions of 400 Mrad γ-irradiated strontium nitrate at different temperatures.

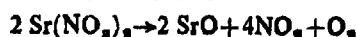
which are accurate to ± 5%, show that whereas the activation energy in the acceleratory stage (E_1) decreases to a small extent on irradiation, that in the decay stage (E_2) increases. That the change upon irradiation is small suggests that the same chemical processes govern the decomposition of both the unirradiated and the irradiated salt. The velocity constants k_1 and k_2 are found to increase with the irradiation dose as seen in Table 2.

TABLE 2 – PROUT-TOMPKINS CONSTANTS FOR DIFFERENT γ-IRRADIATION DOSES

Dose, Mrad	Unirrad.	100	200	300	400
k_1(min^{-1}×10^2)	1.143	1.481	1.667	1.905	2.051
k_2(min^{-1}×10^3)	2.50	3.34	4.17	7.69	8.38

It is known that radiation damage, including chemical damage, anneals on gentle heating of the irradiated crystals[8,9]. But preannealing at 300° for a period upto 100 hr does not change significantly the decomposition characteristics of the irradiated material.

Strontium nitrate melts[14] at 570°, but it is only above 600° that the salt decomposes at a measurable rate[15,16]. It may therefore be assumed that the entire extent of the reaction takes place in the liquid phase. The overall decomposition of the substance occurs as follows :

$$2\,Sr(NO_3)_2 \rightarrow 2\,SrO + 4NO_2 + O_2$$

The autocatalytic nature of the decomposition is attributable to the product SrO. The catalysing action of the nitrite ion in the decomposition of nitrates may be envisaged as follows. The NO_2^- produced during irradiation may act as electron donors and attract oxygen atoms from the neighbouring nitrate ions. The resulting nitrate would then decompose spontaneously.

The Prout-Tompkins[10] analysis for solid decomposition was originally derived on the basis of branching reaction nuclei, i.e., molecules of reactant situated at lattice imperfections mainly on the surface of the solid and possessing a low energy of activation for decomposition[10,11]. Acceleration of the decomposition occurs when these branching chain nuclei form reactive planes in the material producing mechanical strain which may result in the actual disruption of the crystals. Eventually, these planes interfere with one another and after the time of maximum velocity the reaction rate is controlled by the number of undecomposed molecules present in the system. The situation in the autocatalytic decomposition of strontium nitrate occurring in the melt is similar to the above mechanism and thus the Prout-Tompkins analysis is applicable. In fact, autocatalytic reactions of the Prout-Tompkins type require that all the solid products shall be in a position to catalyse all reactant molecules equally throughout the entire course of the reaction, which is not feasible in a solid because of the low mobility of the reacting constituents but is entirely valid for decompositions occurring in the liquid state as in the present case.

Considerable work has been done on the influence of irradiation on the thermal decomposition of solid substances[17]. Generally, the effect of irradiation is to decrease the induction period, if any, and increase the velocity constants for both the acceleratory and decay stages[1,3]. These effects arise from the chemical damage fragments produced by irradiation constituting decomposition nuclei by themselves or from decomposition nuclei formed as a result of the Wigner energy released on recombination of interstitials and vacancies during the period of initial slow reaction. Subsequently, the centres of decomposed material grow and decomposition spikes create strain sufficient to ultimately fracture the crystal, thus creating new reactive

surface where after the reaction proceeds in an acceleratory manner. No such mechanism can be envisaged for liquid phase decompositions. The NO_2^- formed under irradiation catalyse the decomposition of strontium nitrate occurring in the melt. In consequence the induction period is shortened and the velocity constants of both the acceleratory and the decay stages enhanced as in the influence of irradiation on solid decomposition.

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Isomerization of β-pinene in the Vapour Phase over Alumina Catalyst : Influence of Partial Pressure of Nitrogen and Pyridine

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The isomerization of β-pinene in the vapour phase over alumina catalyst has been studied in the presence of nitrogen and pyridine. The isomerization proceeds via two parallel paths, one giving bicyclic products such as α-pinene and camphene and the other giving rise to monocyclic menthadienes such as dipentene, terpinolene, α-terpinene and γ-terpinene. Nitrogen acts as a diluent while pyridine functions as a diluent and as a poison. As a result, it affects the formation of different products to different extent.

The isomerization of β-pinene over alumina follows a second order kinetics. Based on the experimental facts a tentative mechanism, in terms of carbonium ion intermediates, has been proposed.

β-PINENE is a bicyclic mono-olefinic mono-terpene and occurs along with α-pinene in varying proportions in a majority of essential oils derived from Coniferae[1]. The first quality Indian turpentine from *Pinus longifolia* contains about 10% β-pinene, the rest being α-pinene (40%) and 3-carene (50%)[2].

Steinbach *et al*[3] reported the thermal isomerization of β-pinene at 160°, while Sully[4] effected a near quantitative conversion of it into myrcene in the temperature range of 580-750°. Isomerizations of β-pinene over minerals, salts and acids are patented[5]. Verghese[6] investigated the transformations of β-pinene into monocyclic compounds using phosphoric acid.

The present investigation was undertaken to study the influence of nitrogen and hydrogen on the isomerization of β-pinene over alumina, to determine the kinetics of isomerization and to suggest a tentative mechanism for the formation of the various products.

Experimental

Preparation of materials :

Alumina : Alumina was prepared by hydrolyzing aluminium isopropoxide with distilled water[7]. The precipitated aluminium hydroxide was filtered through a Buchner funnel, washed thoroughly with water, cut into cakes, dried at 120° for 24 hr. The material was activated at 550° in a stream of dry air for 24 hr. The activated material was crushed and ground into powder and sieved. The 40-60 mesh fraction was used for all purposes.

β-Pinene : β-Pinene (Hercules Powder Co., USA) was further fractionated and the liquid distilling at 165°/760 mm was collected and stored in brown bottles. The purity was established to be better than 99% by gas chromatography.

Pyridine : Pyridine (B. D H. AnalaR) was refluxed over KOH pellets and distilled through an efficient fractionating column with careful exclusion of moisture and the material distilling at 115.5° was collected. The purity was checked by gas chromatographic analysis.

n-Butylamine : *n*-Butylamine used was obtained from B.D.H. It was purified by fractional distillation (b.p. 78°).

Butter yellow : This was prepared by diazotization of aniline and coupling with dimethylaniline at 4°. The dye was purified by column chromatography, crystallized and recrystallized from *iso*-octane.

Nitrogen : Nitrogen (Indian Oxygen Co.) was purified by passing successively through a silica gel drying tower, a tube containing freshly reduced copper turnings kept at 400°, another silica gel tower and finally through a trap cooled in liquid oxygen.

Apparatus and procedure : The reactions were carried out at atmospheric pressure in a fixed bed pyrex flow type reactor, 50 cm long and 1.5 cm internal diameter. The pre-heater was made in the form of a spiral wound uniformly around the reactor covering half of its length, to ensure complete vapourisation of the liquid before entering

the reactor tube. Above the catalyst (5 g) bed pyrex glass beads (4 mm diameter) were placed to a height of 5 cm. The reactor tube was inserted into a furnace, a cylindrical steel tube of internal diameter 4 cm, coated with a thin layer of asbestos, wound uniformly with a nichrome wire and heated electrically to the requisite temperature.

Nitrogen was carefully metered through a precision Hoke valve and its flow rate was measured with a soap film flow meter. Various partial pressures of pyridine were achieved by mixing it with β-pinene in different proportions.

To regenerate and activate the catalyst, it was heated prior to each run for 8 hr in a current of air at 500° until no oxides of carbon were detected in the exit gas. The reactant liquid was fed into the reactor by a constant speed infusion pump. The liquid products collected for the first 15 min of each run (which normally covers 1 hr) were discarded and analysis was made only of the products collected after this time. This was to ensure the attainment of steady state over the catalyst and also to set right any temperature fluctuations

The liquid products were identified using a Perkin-Elmer infracord spectrophotometer Model-137 and a Perkin-Elmer Vapour Fractometer Model-154 D. They were estimated using a Perkin-Elmer column K, consisting of a two meter column of carbowax on chromosorb. The column temperature for the best resolution within a reasonable time was found to be 115° with hydrogen inlet pressure of 15 psi with TCD detector.

For the identification of different peaks in the chromatogram, retention times for the different compounds were found by introducing authentic samples. For quantitative analysis, synthetic mixtures containing the compounds in varying proportions were introduced and calibration curves relating the concentration with peak heights were drawn. Since the peaks obtained were sharp and symmetrical, peak heights were used as a measure of concentration. All chromatograms for calibration purposes were taken on the same day as a special precaution. Various compounds identified in this investigation are α-pinene, camphene, dipentene, terpinolene, α- and γ-terpinenes. Since the concentration of individual menthadienes is too small, they are grouped together as menthadienes.

The surface area (BET), pore volume, and the average pore radius of the catalyst were determined from low temperature adsorption of nitrogen[8]. The pulse flow technique of Eberly[9,10] was used to measure the heat of adsorption of pyridine in the temperature range of 180-250°. The total acidity of the catalyst was determined by n-butylamine titration method using butter yellow as indicator. All these values are given in Table 1.

TABLE 1—SURFACE PROPERTIES OF ALUMINA

Surface properties	Values
Surface area (BET), m²/g	180.00
Pore volume, ml/g	0.4580
Average pore radius, rÅ	55.00
Heat of adsorption of pyridine, kcal/mole	17.60
Total acidity, meq/g	0.6450

Results and Discussion

Influence of particle size : In order to evaluate the influence of transport processes on the rate of isomerization of β-pinene, the reaction was studi over three different particle sizes and the results a presented in Table 2. This table illustrates tl particle size of the catalyst, their correspondii activities in the isomerization of β-pinene, and tl measured values of the effectiveness factor, which equal to the ratio of the actual reaction rate to tl reaction rate with no diffusion limitation, obtain on the smallest catalyst particle size of 60-80 mest

TABLE 2—INFLUENCE OF PARTICLE SIZE ON THE OVERALL CONVERSION OF β-PINENE

Particle size	Activity of the catalyst (% mole of β-pinene converted)	η measured
Pellets, 5×5 mm	66.00	66/78=0.85
Powder, 40-60 mesh	75.00	75/78=0 96
Powder, 60-80 mesh	78 00	78/78=1.00

It has been pointed out by Weisz[11] that diff sion effects are negligible when η exceeds 0.95. Tl catalyst of particle size 40-60 mesh for which equals 0.96 is almost completely free from diffusi limitation (Table 2). Since the 60-80 mesh cataly gave rise to large pressure drop across the catal bed causing operational difficulties, all the ru were carried out using 40-60 mesh catalyst.

Effect of partial pressure : The overall conve sion of β-pinene at various partial pressures pyridine at 232° is illustrated in Fig. 1. The resu obtained in presence of inert diluent nitrogen also plotted in the same figure for compariso The distribution of products in the presence nitrogen and pyridine is given in Figs. 2 and respectively. In the presence of nitrogen, the ove all conversion of β-pinene increases with increasi partial pressure of β-pinene upto 0.8 atm (Fig. Above this value the conversion is independent it. The catalytically active sites are incomplete filled below 0.8 atm and saturated with respect β-pinene molecules beyond this value and hen increase of partial pressure of β-pinene has effect on the rate.

Pyridine suppresses the rate of isomerizati more significantly than nitrogen. For instan the amount of β-pinene undergoing conversion their absence is 80%. At a partial pressure of 0. atm, the amounts reacted are reduced to 77% a 52% by nitrogen and pyridine, respectively. Nitr gen acts only as a diluent. Pyridine being a ba adsorbs preferentially to β-pinene over bo Brönsted and Lewis acid sites with chemic

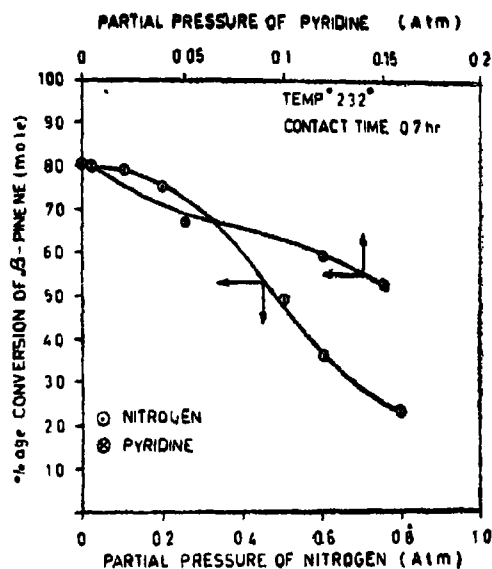



Fig. 1. Effect of partial pressure of nitrogen and pyridine on the overall conversion of α-pinene Temp 232°, contact time=0.70 hr.

reactions. It is presumed that it neutralizes the Brönsted acid sites with the formation of pyridinium ion and coordinates with the electron deficient aluminium atom (Lewis acid). As a result of these two reactions, the active sites essential for the isomerization of β-pinene are not available and therefore the conversion falls significantly.

Increase of partial pressure of nitrogen affects the formation of products almost equally (Fig. 2). As the conversion of β-pinene decreases with increasing partial pressure of nitrogen, the concentration of products falls.

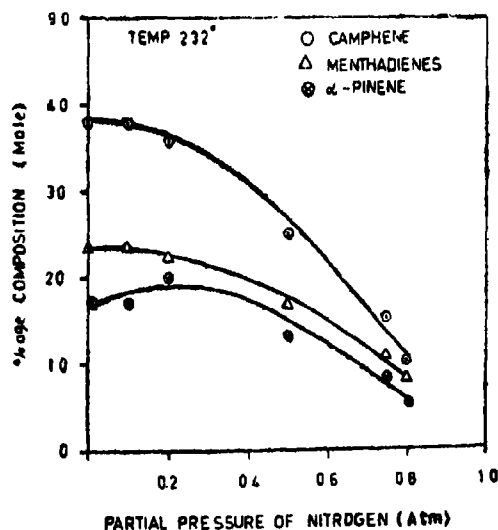



Fig. 2. Effect of partial pressure of nitrogen on formation of products. Temp. 232°; contact time=0.70 hr.

Pyridine, unlike nitrogen, suppresses the formation of different products differently (Fig. 3). For

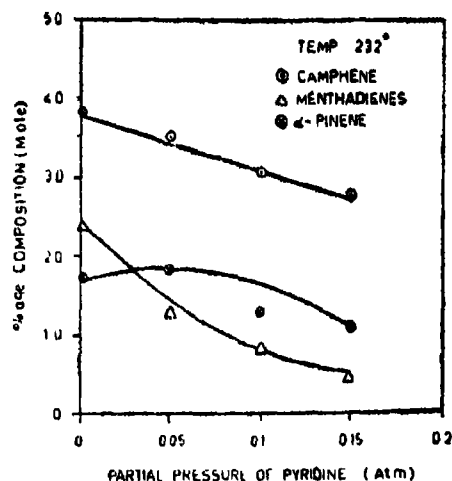



Fig. 3. Effect of partial pressure of pyridine on the formation of products. Temp. 232°, contact time=0.70 hr.

instance, in the absence of pyridine the concentrations of α-pinene, menthadienes and camphene in the liquid products are 27, 24 and 38%, respectively. Increase in the partial pressure of pyridine from 0 to 0.15 atm decreases these products to 11, 4 and 28%, respectively. Pyridine inhibits the formation of menthadienes to a greater extent than the other two products. From these observations it may be conclude that pyridine inhibits the skeletal isomerization of β-pinene (leading to the formation of menthadienes) more significantly than the double bond isomerization (that gives rise to α-pinene). Camphene formation involving the bridged ring structure is also less affected.

Kinetics. The kinetics of isomerization of β-pinene over alumina has been found to follow a second order kinetics by plotting $\left(\frac{1}{1-x_A}\right)$ against contact time, W/F_A, where W is the weight of catalyst and F_A is the flow rate of β-pinene per gram of the catalyst (Fig. 4). The rate constants computed from the slopes of the straight line plots are 187.15 and 547.33 litres $mole^{-1}$ $hour^{-1}$ at 180 and 232°, respectively. The activation energy was calculated to be 5.1 kcal/mole.

Mechanism · It has been well established that alumina surface contains both Brönsted and Lewis acid sites. Several mechanisms have been proposed for the isomerization of olefins over solid acid catalysts. These include the carbonium ion theory of Whitmore[12] and hydrogen switch mechanism of Turkevich and Smith[13]. Pines and Haag[14] have proposed that the isomerization proceeds through an intermediate π-complex of the olefin and a proton from the catalyst. All these mechanisms assume proton addition to the olefinic double bond accompanied by a subsequent or simultaneous proton elimination from another part of the carbonium ion thus formed.

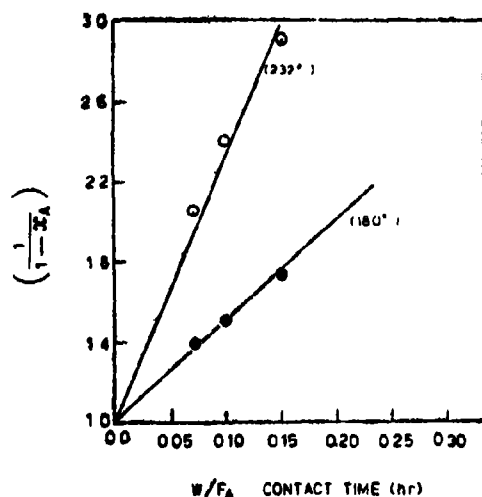
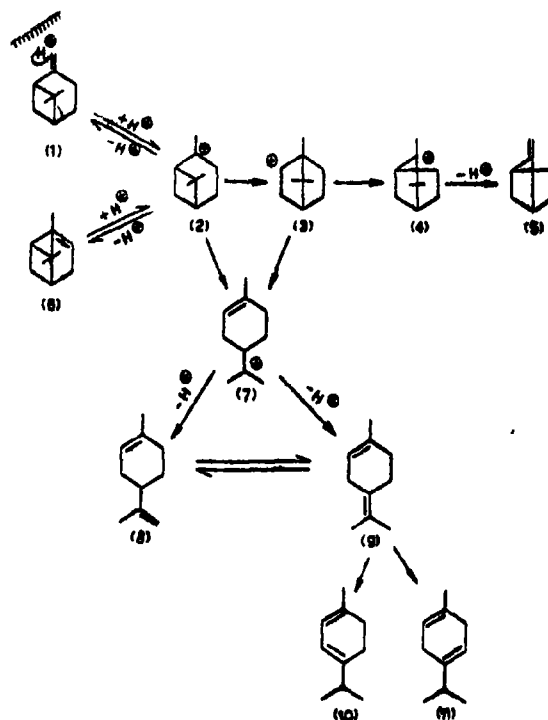



Fig. 4. Second order plots, temp. 180° and 232°.

Carbonium ions on the surface of solid acid catalysts have been identified by Leftin and Hermana[15]. Osaki and Kimura[16] have suggested a proton donor-acceptor mechanism for butene isomerization over solid acid catalysts, either by Brönsted acid sites on the surface of the catalysts or by the carbonium ions formed by the adsorption of olefins on the Lewis sites serving as proton donors.

The isomerization of β-pinene (1) over alumina will be interpreted in terms of carbonium ion intermediates adsorbed on the catalyst surface. It undergoes three types of reactions as outlined in the scheme. Initially the catalyst surface interacts with the double bond of β-pinene molecule resulting in the formation of the carbonium ion (2). This stable tertiary carbonium ion rearranges to a less stable secondary carbonium ion (3) by ring expansion. Carbonium ion (3) undergoes Wagner-Meerwein rearrangement resulting in the formation of camphene (5) through a stable tertiary carbonium ion (4).

Carbonium ion (2) changes into a stable allylic system by elimination of a proton leading to the formation of α-pinene (6). Carbonium ions (2) and (3) may also rearrange to monocyclic carbonium ion (7) by ring opening. This on subsequent elimination of a proton from the appropriate carbon atom gives dipentene (8) and/or terpinolene (9). The exocyclic double bond in terpinolene further isomerizes to endocyclic positions giving rise to α-terpinene (10) and γ-terpinene (11).

Scheme

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Vibrational Analysis of Glyoxal-h_2-d_2 and hd

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A complete vibrational analysis has been made for glyoxal-h_2, -d_2 and hd. A reasonable set of force constants has been obtained using the general valence force field by the Wilson's F-G matrix method. Using these values other important molecular constants such as mean amplitudes of vibration, generalised mean-square amplitudes of vibration, shrinkage constants, Coriolis coupling constants, centrifugal distortion constants and thermodynamic properties have been computed and presented. A comparison is made between the values obtained in the present investigation and the values available in literature.

TRAMER and co-workers[1] recorded gas phase emission spectra of glyoxal-h_2 and -d_2, presenting in the case of the deuterated species some weak bands not reported earlier. From the frequency of combination bands of the ir spectrum of these molecules by Cole and Osborne[2], several bands can be assigned. Cossart-Magos[3] has made the normal coordinate analysis of these molecules on the basis of valence force field. A previous calculation[4] of the fundamental frequencies of glyoxal-h_2 and -d_2 used a modified Urey-Bradley force field. Cossart-Magos[3] has introduced two more interaction constants which were absent in the Urey-Bradley force field. The structural parameters used for the present investigation have been taken from the work of Kuchitsu *et al*[5] conjugating electron diffraction and spectroscopic data. The normal modes of vibration are distributed among the two symmetry species as $5A_g+4B_u$. However, potential energy constants have been reinvestigated using the general valence force field. On the basis of GVFF, the mean square amplitudes of vibration, the generalised mean square amplitudes of vibration, shrinkage constants, Coriolis coupling constants, centrifugal distortion constants and thermodynamic quantities have been computed for these molecules.

The molecular configuration, numbering of atoms and the orientation of the Cartesian coordinate axes are shown in Fig. 1.

Methods of calculation :

The potential energy matrix F has been derived relating to the general valence force field. The kinetic energy matrix G has been obtained by making use of the geometrical parameters according to the relation $G=BM^{-1}B'$, where M^{-1} is a diagonal matrix of the reciprocal masses and B is the transformation matrix from Cartesian displacement coordinates to internal coordinates. By solving the
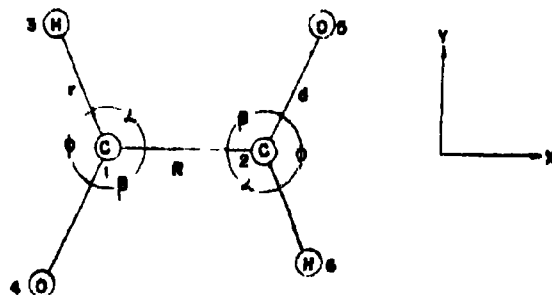
Fig. 1. The molecular configuration, numbering of atoms and the orientation of the Cartesian coordinate axes of glyoxal-h_2, -d_2 and hd.

secular equation[6] $|FG-E\lambda| = 0$, a reasonable set of force constants has been evaluated.

The symmetrised mean square amplitude matrix Σ has been calculated by L-matrix method[7]. The generalised mean square amplitudes $\langle(\Delta z)^2\rangle$, $\langle(\Delta y)^2\rangle$ and $\langle(\Delta x)^2\rangle$ have been computed by deriving relevant expressions following the method of Morino and Hirota[8]. The shrinkage constants have been determined from the perpendicular mean square amplitudes by the method suggested by Morino *et al*[9].

Applying Jahn's rule[10], the non-vanishing zeta values are found to be of the type ζ^z arising from the coupling $A_g\times A_g$ and $B_u\times B_u$. These constants have been estimated using the matrix relation,

$$\zeta^\alpha = L^{-1}C^\alpha \tilde{L}^{-1}$$

where L is the normal coordinate transformation matrix and C^α ($\alpha=x, y, z$) is the skew symmetric matrix obtained by the vector method of Meal and Polo[11].

Since the bonds between the atoms in a molecule are not rigid, the interatomic distances will vary

with the speed of rotation giving rise to centrifugal distortion. The centrifugal distortion constants have been computed with the aid of the relations given by Kivelson and Wilson[18] and by Cyvin *et al*[19].

Results and Discussion

The internal force constants obtained using GVFF are presented in Table 1 along with the values calculated by Cossart-Magos[9] for comparison. The agreement is found to be quite satisfactory. The force constant f_r is found to be about three times the force constant f_d. Also the force constant f_α is smaller than f_β. It has been shown by Ohwarda[14] that the interaction force constant of highly delocalised bond molecule tends to take a large +ve value while that of highly localised bond molecule, a −ve value. Hence the sign of the force constant is a measure of the electron localization or delocalization in a molecule. The values evaluated in the present investigation are made use of for the calculation of other molecular constants.

TABLE 1—THE INTERNAL FORCE CONSTANTS OF GLYOXAL AND ITS ISOTOPES

(m.dyne/A)

Designation	values	values from Ref. (3)
f_r	4.890	4 896
f_d	12.626	12 668
f_R	4.700	4 700
f_{rr}	0.010	
f_{dd}	−0.175	
f_β	0.588	0 548
$f_{\beta\beta}$	−0.018	
f_α	0.472	0.551
$f_{\alpha\alpha}$	−0.018	
$f_{d\beta}$	−0.495	
$f_{d\alpha}$	0.809	
f_R	−0 094	−0.128
$f_{R\alpha}$	0.260	0.884

The mean square amplitude quantities calculated at 300 K are given in Table 2. The generalised mean square amplitudes of vibration and the shrinkage constants are listed in Table 3. The parallel mean square amplitudes $\langle(\Delta z)^2\rangle$ compare very well with the mean square amplitude quantities (σ). Since $f_r < f_d$, $\sigma_r > \sigma_d$. It can also be seen that since f_d is very large, the mean square amplitude σ_d is found to be very small. Also the natural and practical shrinkages are found to be equal.

TABLE 2—MEAN-SQUARE AMPLITUDES OF VIBRATION OF GLYOXAL AND ITS ISOTOPES AT 300 K(Å²)×10⁻⁴

Designation	$C_2H_2O_2$	$C_2D_2O_2$	C_2HDO_2
σ_r	69.201	54 958	66.610
σ_d	14.479	21.672	17 687
σ_R	25.836	29 037	25.617
σ_β	111.870	75 878	102 810
σ_α	56.899	67.458	45 076
σ_{rr}	−1.682	4.967	25.770
σ_{dd}	0.340	−2.119	−0.520
$\sigma_{\alpha\alpha}$	16.340	22.195	1.770
$\sigma_{\beta\beta}$	−29.818	11 197	32.859
σ_{rd}	−1.180	−5.500	−7.570
$\sigma_{r\beta}$	4.360	−10.004	−14.148
σ_{Rr}	−2.170	−4.780	−1.900
σ_{rd}	2 850	26.540	−8.480
$\sigma_{d\beta}$	7 260	8.760	9.880
σ_{Rd}	−5 990	−4.960	−5.810
$\sigma_{d\alpha}$	−4.880	−15.880	−2.870
$\sigma_{R\alpha}$	−7.260	−6.630	−4.900
$\sigma_{\beta\alpha}$	−4.100	−25.801	−13.582
$\sigma_{R\beta}$	−9.760	−5.590	−9.060

The Coriolis coupling coefficients are presented in Table 4. These coefficients facilitate the analysis of vibration-rotation spectra. The following zeta square sum rule is found to be satisfied for the $A_g \times A_g$ coupling:

$$\zeta^2_{1,2}+\zeta^2_{1,3}+\zeta^2_{1,4}+\zeta^2_{1,5}=1$$

The centrifugal distortion constants are listed in Table 5. As there is no experimental data available

TABLE 3—GENERALISED MEAN-SQUARE AMPLITUDES OF VIBRATION (Å²)×10⁻⁴ AND SHRINKAGE CONSTANTS (A) OF GLYOXAL AND ITS ISOTOPES

Atom pair	Designation	$C_2H_2O_2$	$C_2D_2O_2$	C_2HDO_2	Shrinkage constants
C−O	$\langle(\Delta z)^2\rangle$	14 471	21.414	17.720	
	$\langle(\Delta y)^2\rangle$	59 248	66 828	62 437	
	$\langle(\Delta z\Delta y)\rangle$	0.616	−9.700	2.683	
C−H	$\langle(\Delta z)^2\rangle$	69 109	54.960	66 010	
	$\langle(\Delta y)^2\rangle$	240.180	140.070	170.868	
	$\langle(\Delta z\Delta y)\rangle$	−8 879	−4.396	6.438	
C−C	$\langle(\Delta z)^2\rangle$	25 980	29.037	25.617	
	$\langle(\Delta y)^2\rangle$	107.891	97.638	102.814	
	$\langle(\Delta z\Delta y)\rangle$	−0.494	−4.218	−6.124	
C H	$\langle(\Delta z)^2\rangle$	52.429	26.188	64.899	
	$\langle(\Delta y)^2\rangle$	145.284	90 005	167.778	
	$\langle(\Delta z\Delta y)\rangle$	61.702	50.856	110.872	$\delta C_2\cdots O_4$ = −0 04039 − 0.04565 − 0.03591
C ..O	$\langle(\Delta z)^2\rangle$	22.672	20.078	23.884	$\delta O_4\cdots H_2$ = −0.03078 − 0.03588 − 0.03616
	$\langle(\Delta y)^2\rangle$	86 186	55.467	28.742	
	$\langle(\Delta z\Delta y)\rangle$	17.854	21.629	11.889	

TABLE 4—CORIOLIS COUPLING CONSTANTS OF GLYOXAL AND ITS ISOTOPES

Designation	$C_2H_2O_2$	$C_2D_2O_2$	C_2HDO_2
		Coupling $A_g \times A_g$	
ζ^x_{12}	0.22978	0.26674	0.26478
ζ^z_{13}	0.92950	0.74499	0.72619
ζ^x_{14}	−0.00470	−0 09529	0 04325
ζ^z_{15}	0.28923	0.60438	0.63950
ζ^x_{23}	−0 02588	0 80994	−0.17937
ζ^z_{24}	0.69161	0.59106	0.83205
ζ^z_{25}	−0.25844	−0 84665	−0.31335
ζ^z_{34}	0.05024	0 27566	0.11695
ζ^z_{35}	0.16566	0.23569	0.58959
ζ^z_{45}	0 66714	0.55609	0.43699
		Coupling $B_u \times B_u$	
ζ^z_{67}	0 16286	0.24054	0 29526
ζ^z_{68}	0.96171	0.97132	0.95419
ζ^z_{69}	· 0 30432	0.02406	−0.04679
ζ^z_{78}	−0 64662	0 02416	−0 04874
ζ^z_{79}	−0 93848	−0.97041	−0.97074
ζ^z_{89}	0 16473	0 24003	0.29764

for centrifugal distortion constants, on comparison could be attempted.

TABLE 5—CENTRIFUGAL STRETCHING COEFFICIENTS (M Hz) OF GLYOXAL AND ITS ISOTOPES

	$C_2H_2O_2$	$C_2D_2O_2$	C_2HDO_2
D_J	0.021006	0 018905	0.019379
D_K	0.023445	0.021074	0 021620
D_{JK}	−0.043366	−0 039030	−0.039978
R_5	−0.004201	−0.003795	−0 003930
R_6	−0.002033	−0.001356	−0.001559
δ_J	−0.011451	−0 010688	−0.010706

Tables 6-8 give the values of the heat capacity, free energy, heat content, and entropy computed from the observed vibrational frequency data, over the range 100-1000K at intervals of 100K. The calculations are all based on a rigid rotor harmonic oscillator model with no interaction between the vibrational and rotational energies. The quantities evaluated are the combined translational rotational and vibrational contributions.

TABLE 6—THERMODYNAMIC FUNCTIONS OF $C_2H_2O_2$

T(K)	S	F	C_p	H
100	52.27162	44.28551	8.15252	7.98611
200	58.15651	49.89556	8.92176	8 26095
273	61.01304	52.50282	9.46042	8 51022
300	61.91487	53.31010	9.66482	8 60478
400	64.79958	55 83408	10 44552	8.96550
500	67.21454	57.87513	11.21869	9.33941
600	69.32876	59.61370	11 93254	9.71506
700	71.20327	61.13487	12.54190	10.06840
800	72.92414	62.50314	13.10920	10 42100
900	74.50392	63 75563	13.58370	10.74820
1000	75.96335	64.90725	13.99180	11.05610

TABLE 7—THERMODYNAMIC FUNCTIONS OF $C_2D_2O_2$

T(K)	S	F	C_p	H
100	52.52730	44.52650	8 20558	8.00080
200	58.46950	50.15779	9.05582	8 31176
273	61.38428	52.78565	9.72457	8.59863
300	62.31166	53.60235	9.96858	8.70931
400	65.30319	56.16677	10 88919	9.14141
500	67.83095	58.25348	11.75101	9.57747
600	70.02051	60 01901	12.53400	10.00150
700	72 02529	61.61139	13.18430	10 41390
800	73 82231	63.02656	13.74195	10 79580
900	75.46160	64.31400	14.21030	11.14760
1000	76.98467	65.50957	14.58600	11.47510

TABLE 8—THERMODYNAMIC FUNCTIONS OF C_2HDO_2

T(K)	S	F	C_p	H
100	53.78674	45.79274	8.18181	7.99400
200	59.70412	51.41496	8.99168	8.28915
273	62.58837	54.03270	9.58574	8.55567
300	63.50303	54.84456	9.81822	8.65847
400	66.44200	57.39019	10.66200	9.05401
500	68.91188	59 45503	11.47710	9.45680
600	70.62565	60.99957	12.00542	9.62608
700	73.00495	62.76175	12.87090	10.24320
800	74.76152	64.15462	13.42370	10 60690
900	76.37686	65.42686	13.89520	10.95000
1000	77.89043	66.59183	14.28710	11.29660

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Behaviour of Vanadyl Porphyrin Complexes on TLC

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The behaviour of a vanadium porphyrin complexes concentrate obtained from Darius crude oil has been studied on tlc using a variety of solvent combinations and silica gel as the adsorbent. Reasonably good separation has been achieved with three solvent combinations in one dimensional run. Acetonitrile and acetonitrile, benzene, cyclohexane (3 : 5 : 11.3) afforded the best results in a double run.

EXTENSIVE work has been done on the behaviour of porphyrins from biological sources on paper and thin layer chromatography. Various solvent systems have been recommended for the separation of porphyrin dicarboxylic acids and methyl esters of porphyrins, chlorins and related compounds on tlc[1-7]. Two dimentional chromatography was successfully carried out by Elder on porphyrin methyl esters which were poorly differentiated in one dimensional systems[8]. Besides silica gel, other adsorbents tried were talc[9-10] and cellulose[11]. Application of paper and thin layer chromatography in the study of porphyrins has been reviewed by Falk[12] and Doss[13], respectively. Work on the tlc behaviour of metal porphyrin complexes, on the other hand, has been limited to the study of chlorophylls, Cu and Zn complexes of certain porphyrins[4] and synthetic samples of V, Ni and Cu-complexes of tetraphenyl porphins[14].

As regards petroporphyrins, paper chromatography has been frequently employed for understanding the composition of porphyrin aggregates (demetallated porphyrins)[15,16]. Little information, however, is available about the behaviour of these porphyrins on tlc. Only recently Didyk *et al*[17] have reported the isolation of five prophyrins from La Paz, a cretaceous crude oil, using this technique. To the best of the present authors' knowledge there is no report on the behaviour of petroporphyrins (metal porphyrin complexes from petroleum) on tlc. In course of our work on the isolation of metal porphyrin complexes from Darius crude, a crude from off-shore field in Iran, a study of the behaviour of petroporphyrins concentrate on tlc was necessary for understanding its composition.

Experimental

Materials : The vanadium complex concentrates were prepared from Darius crude (Table 1). This crude is from off-shore field in Iran and has the highest metal content [vanadium : 25 and nickel : 10 ppm (Table 2)] among all the crude oils presently being processed in India. The crude, topped upto 140°, was deasphalted using propane. The asphalt, thus obtained, was adsorbed on kieselguhr and preferentially extracted with acetonitrile containing small amounts of benzene affording the initial metal porphyrin complexes concentrate. The vanadium porphyrin complex concentrate (Conc. D_1 ; Fig. 1) was prepared by elution chromatography using silica gel. Vanadium prophyrin complexes have characteristic visible spectra[18,19]. This property has been used to determine the presence of these complexes in various fractions. Similar techniques for isolation and characterisation have been used by earlier workers as well[20,21]. Fig. 2 illustrates the visible spectrum of the concentrate prepared.

All the solvents used were of L. R. quality. TLC plates (5×20 cm ; thickness 0.3 mm) were prepared by using a slurry of silica gel G (E. Merck) in water and later activated at 110-20° for 1 hr. The oxalic acid coated plates were prepared by

TABLE 1—CHARACTERISTIC OF DARIUS CRUDE

Density, d_4^{15}	0.852
API gravity	34.49
RVP at 37.8°, Kg/cm²	0.34
Kinematic viscosity, cS at 37.8°	5.06
50°	3.98
Pour point, °C	−30
Carbon residue conradson, %wt	3.8
Sulphur, total %wt	2.4
Characterisation factor	11.9
Water content, %v	Trace
Sediment, %wt	0.0007
Salt content, %wt	0.0008
lbs/1000 bbl	1.0
Ash, %wt	0.006
Calorific value, cal/g	10.800

TABLE 2—METAL CONTENT OF THE CRUDE (ppm)

Vanadium	25 0
Nickel	10.0
Iron	2.0
Copper	0.5
Magnesium	Not detected

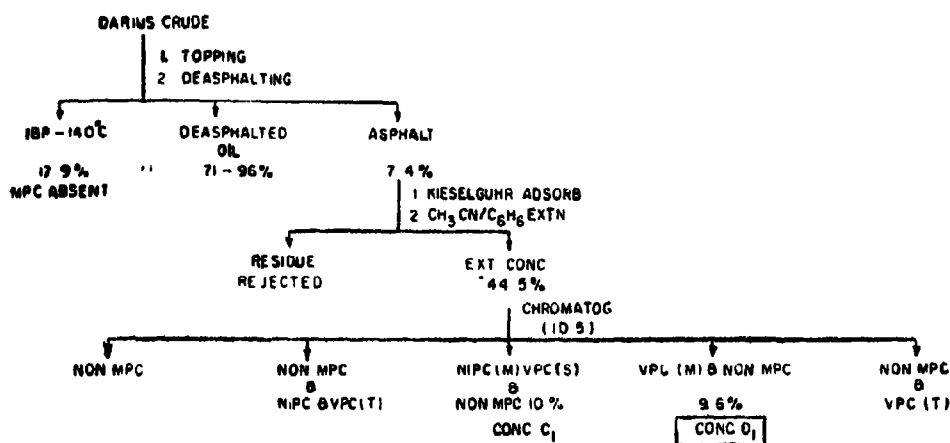
* Author for correspondence.

* VPC VANADIUM PORPHYRIN COMPLEXES, NIPC NICKEL PORPHYRIN COMPLEXES, NON MPC NON METAL PORPHYRIN COMPLEXES
* ADSORBENT FOR CHROMATOG SILICA GEL, A/S IN BRACKET M' MAJOR, S SMALL, T TRACES

Fig. 1. Preparation of VPC concentrate from asphalt.

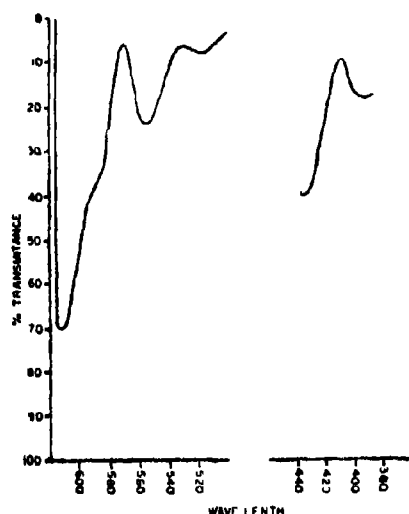



Fig. 2. V-Prephyrin complexes concentration in benzene. conc. 0.68% (w/v) conc. 0.68% (w/v)

making the slurry in 0.5 N oxalic acid solution and for buffered plates in acetic acid (0.2 M; 48 ml) and sodium acetate (0.2 M; 12 ml) [pH 4.05]. The sample was applied in acetone or benzene solution. The time for saturation of the chamber and development of the plate was 30 and 10 min, respectively. The temperature varied from 25 to 30°. The solvent was allowed to run only 8 cm from the base. The air dried developed plates were sprayed with cyclohexane and viewed under uv light (350 nm). Esterification of the sample (in methanol) was carried out using ethereal solution of diazomethane.

Tables 3 and 4 list the various solvent systems tried, the resolution obtained and the colour and R_f values of the spots. Fig. 3 shows how the spots appeared on the chromatograms.

Results and Discussion

Use of solvent combinations already reported in the literature as developing solvents for porphyrins did not yield encouraging results. It was soon

B—Blue P—Pink V—Violet Br—Brown R—Red Y—Yellow

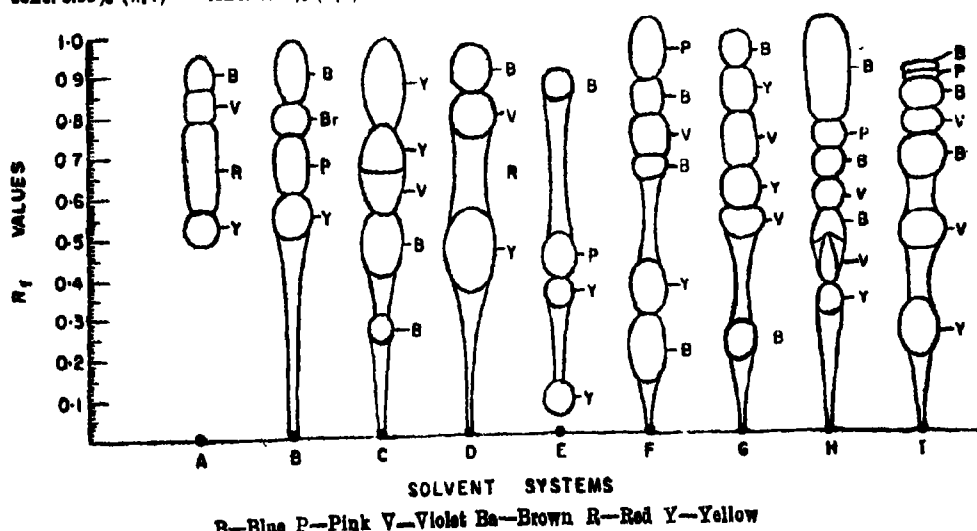



Fig. 3.

TABLE 3—TLC OF VOPC CONC.

Solvent system	Composition	TLC Pattern	R_f	Appearance under uv light
A	Acetone (1)-	4 spots and	0.53	Yellow
	n-Heptane (1)	residue	0.67	Red
			0.83	Violet
			0.91	Blue
B	Acetonitrile (3)-	4 spots, 1	0.55	Yellow
	Benzene (5)	tail and	0.68	Pink
	Cyclohexane (11.3)	residue	0.80	Brown
	in NH_3-atmosphere		0.92	Blue
C	Acetonitrile	5 spots, 2	0.27	Blue
		tails and a	0.48	Blue
		residue (on	0.62	Violet
		oxalic acid	0.72	Yellow
		coated plate)	0.88	Yellow

TABLE 4—TLC OF ESTERIFIED VOPC CONC.

Solvent system	Composition	TLC pattern	R_f	Appearance under uv light
D	Acetone (1)-	4 spots, 1 tail	0.46	Yellow
	n-Heptane (1)	and residue	0.66	Red
			0.80	Violet
			0.91	Blue
E	Acetonitrile (3)-	4 spots, 2 tails	0.09	Yellow
	Benzene (9)-	and residue	0.36	Yellow
	Cyclohexane (7.2)		0.45	Pink
			0.87	Blue
F	Acetonitrile	6 spots, 2 tails	0.21	Blue
		and residue	0.37	Yellow
			0.67	Blue
			0.75	Violet
			0.84	Blue
			0.96	Pink
G	Cyclohexane (2)-	6 spots, 2 tails	0.24	Blue
	Ethanol (1)	and residue	0.54	Violet
			0.62	Yellow
			0.74	Violet
			0.87	Yellow
			0.96	Blue
H	Cyclohexane (2)	7 spots, 1 tail	0.34	Yellow
	Benzene (1)-	and residue	0.43	Violet
	Ethanol (1)		0.53	Blue
			0.60	Violet
			0.68	Blue
			0.75	Pink
			0.91	Blue
I	(C) Acetonitrile	7 spots, 3 tails		
		and residue	0.26	Yellow
	(B) Acetonitrile (3)-		0.51	Violet
	Benzene (5)-		0.70	Blue
	Cyclohexane (11.3)		0.78	Violet
			0.85	Blue
			0.90	Pink
			0.96	Blue

realized that solvent combinations, degree of saturation of the chamber, amount of the sample spotted and the distance moved by it were the various factors affecting the separation. Moreover, the metal porphyrin complexes lacked the sensitive fluorescence of the uncomplexed pigments and their characteristic colour could be detected at relatively high levels of concentration where the danger of tailing exists. Use was, therefore, made of an indirect method of sprying the air dried developed plates with cyclohexane before viewing them under uv light. *Iso*-octane or a dilute solution of fluoranthene in cyclohexane[16] was found to be equally effective amongst the various solvent combinations attempted for studying the behaviour of the petroporphyrins concentrate on tlc. The best resolution, however, was obtained with acetone-*n*-heptane (1 : 1), affording four spots and a residue. The solvent was allowed to move a distance of only 8 cm as beyond this distance the spots had a tendency to diffuse. The spots were blue, brown, pink and yellow in colour with R_f values of 0.91, 0.83, 0.67 and 0.53, respectively. The major problem in the chromatography of the metal poryhyrin complexes was their tendency to tail. To overcome this difficulty ammonia atmosphere[22] and oxalic acid coated plates[23] were tried. Acetonitrile-benzene-cyclohexane (3 : 5 : 11.3) and acetonitrile gave satisfactory results with the former and the latter systems, respectively but were in no way superior to acetone-*n*-heptane (1 : 1) (cf. Table 3). Sodium acetate buffered plates[24] did not bring results.

As petroporphyrins are known to occur sometime as carboxylic acids[18], the esterified sample (diazomethane) was subjected to extensive thin layer chromatography using a number of solvent combinations. Table 2 lists the various solvent systems affording a reasonably good resolution of the esterified petroporphyrin concentrate. Resolution was greatly improved by the use of solvents systems like acetonitrile ; cyclohexane-ethanol (2 : 1) and cyclohexane-benzene-ethanol (2 : 1 : 1) resolving the starting material into seven spots, two tails and a residue. The spots were of different colours and nicely distinguishable from one another. The last two solvent combinations probably gave the best resolution but suffered from homogeneity problem at lower temperature.

Another attempt to further improve the resolution, if possible, was made by running the tlc plates in two solvent systems. The sample was run in the first solvent system (8 cm with respect to the solvent), the plate air dried and return the same distance in the second solvent in the same direction. Acetonitrile (in the first run) and acetonitrile-benzene-cyclohexane (3 : 5 : 11.3) in the second run resolved the esterified concentrate into seven spots, three tails and a residue. This combination was found to be the best among all the solvent systems tried.

Conclusion : The petroporphyrins concentrate prepared from Darius crude could be resolved satisfactorily on silica gel plates using acetone-*n*-heptane (1 : 1) as the developing solvent. Degree of saturation of the chamber, amount of the sample spotted and the distance moved by it were the various factors affecting the separation. The resolution could be improved considerably by running the esterified sample in acetonitrile ; cyclohexane-ethanol (2 : 1) and cyclohexane-benzene-ethanol (2 : 1 : 1) in one dimension. Best results were, however, obtained with acetonitrile and acetonitrile-benzene-cyclohexane (3 : 5 : 11.3) in a double run.

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Kinetics of Chromic Acid Oxidation of Phenacyl Bromides (ω-Bromoacetophenones)

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The kinetics of the oxidation of phenacyl bromide (ω-bromoacetophenone) and several substituted phenacyl bromides by chromic acid have been investigated in 90% acetic acid (v/v). The reaction rate is first order with respect to the [oxidant] as well as to the [substrate]. A decrease in the proportion of acetic acid in the reaction mixture decreases the rate. The reaction rate decreases in the presence of added Mn(II) ions. The presence of complexing agents like succinic acid and piperidine also decrease the rate. The value of ρ^+ has been found to be -0.20 from a linear correlation of the rate constants with Brown's σ^+ parameter. The data conform to the mechanism involving an enol intermediate.

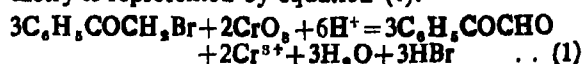
CHROMIC acid is one of the most versatile oxidising agents[1]. Kinetics of oxidation of many alicyclic and aliphatic ketones by chromic acid have been reported by a number of workers[2-5]. Similar studies on α-haloketones are not found in the literature. This prompted us to study the kinetics of oxidation of phenacyl bromide and substituted phenacyl bromides to obtain more informations on the mechanism of oxidation.

Experimental

Materials and method : The substrates employed were unsubstituted, *p*-methoxy, *p*-methyl, *m*-nitro and *p*-nitro phenacyl bromide. These were prepared and purified by the methods available in literature[6-7]. Perchloric acid (60% Baker, AnalaR) was used as a source of H^+ Pure acetic acid (b.p. 118°), free from oxidisable impurities, was obtained by warming acetic acid (AnalaR, 40 g) and acetic anhydride (AnalaR, 160 ml) slowly to just below the reflux temperature for 0.5 hr, the mixture was then heated under reflux for 0.5 hr and then distilled through a fractionating column containing glass helices. The ionic strength was maintained by adding sodium perchlorate (AnalaR, B.D.H.). Triple distilled water was used for dilution.

Kinetic measurements : Rate measurements were carried out at constant temperature (±0.1°). The solvent used was 90% aqueous acetic acid (v/v) containing 0.2*M* $HClO_4$. The reaction was followed by withdrawing aliquots of the reaction mixture at known intervals of time, quenching the reaction by adding slight excess of ferrous ammonium sulphate and titrating the residual Fe(II) against standard $K_2Cr_2O_7$ solution using barium diphenyl sulphonate as an indicator. Diffused light did not affect the rate constants. The rate constants were computed with an accuracy of 1-2% in duplicate runs.

Stoichiometry : The stoichiometry of the reaction was determined by allowing reaction mixtures containing excess of chromic acid to stand for 3 to 4 days at 30° until there was no change of Cr(VI) concentration. The unreacted oxidant was then estimated by the usual procedure. The stoichiometry is represented by equation (1).

$$3C_6H_5COCH_2Br+2CrO_3+6H^+=3C_6H_5COCHO+2Cr^{3+}+3H_2O+3HBr \quad (1)$$

The tlc pure product isolated was characterised as phenyl glyoxal[8], yellow liquid, b.p. 96°.

Rate law : The reaction is first order with respect to the [phenacyl bromide] as well as the [oxidant] (Table 1). The rate of the reaction increases with the increase in [$HClO_4$] (Table 2). Under the condition of constant ionic strength the first order rate constant (k_1) is proportional to [H^+].

TABLE 1—DEPENDENCE OF RATE ON [CrO_3] AND [*m*-NITRO PHENACYL BROMIDE]

[$HClO_4$]=0.2 *M*, μ=1 *M*, Solvent=90% Acetic acid (v/v), Temp.=35°

[*m*-Nitrophenacyl bromide]×10³ *M*	[CrO_3]×10⁴ *M*	$k_1\times10^5$ sec⁻¹	$k_1\times10^3$ mole⁻¹ sec⁻¹ / [*m*-Nitrophenacyl bromide]
10.0	1.0	3.17	
10.0	2.0	4.50	
10.0	4.0	5.80	
10.0	5.0	7.90	
10.0	10.0	8.82	
10.0	15.0	8.40	
10.0	20.0	8.65	
10.0	25.0	8.70	
10.0	30.0	8.75	
5.0	10.0	4.20	8.40
10.0	10.0	8.82	8.82
20.0	10.0	16.90	8.45
30.0	10.0	24.80	8.26
40.0	10.0	33.10	8.27
50.0	10.0	42.20	8.27

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TABLE 2—DEPENDENCE OF RATE ON [ACID]

$[CrO_3]=0.001\ M$; [*m*-Nitro phenacyl bromide]=0.01 *M*, Solvent=90% Acetic acid (v/v), $\mu=1\ M$, Temp.=35°

$[HClO_4]$*M*	$k_1\times10^5\ sec^{-1}$	$k_1/[H^+]\times10^4$
0.1	4.25	0 425
0.2	8.82	0.441
0.3	13.02	0.434
0.4	17.28	0.432
0.5	21.46	0.429
0.6	25.90	0.447
0.7	28.45	0.441
0.8	33.76	0.442
0.9	40.80	0.447

Solvent effect : The reaction was studied in various acetic acid-water binary mixtures. An increase in the proportion of acetic acid increases the rate of oxidation (Table 3). This is probably due to the lowering of dielectric constant (D) of the medium[9], which favours reaction involving protonation. In acetic acid medium, H_2CrO_4 exists as acetochromic acid, $CH_3COOCrO_3H$, or its protonated form $CH_3COOCrO_3H_2^+$ which are assumed to be strong acids and much more powerful oxidising agents than chromic acid[10-12]. The plot of log k_1 versus 1/D is linear as expected for ion-dipole reactions. The same argument has also been advanced by Venkatasubramanian[13]. Further, the extent of enolization of the ketone is enhanced by increasing the proportion of acetic acid and hence the rate increases.

Effect of added Mn(II) · The reaction rate decreases in the presence of added Mn(II) ions (Table 4). The same observation has been noted

TABLE 3—EFFECT OF SOLVENT COMPOSITION ON THE RATE OF CHROMIC ACID OXIDATION OF PHENACYL BROMIDE

$[CrO_3]=0.001\ M$, [*m*-Nitro phenacyl bromide]=0.01 *M*, $[HClO_4]=0.4\ M$, $\mu=1\ M$, Temp.=35°

%HOAc (v/v)	$k_1\times10^5\ sec^{-1}$
70	4.79
75	5.02
80	6.90
85	8.05
90	17.28
95	20.72

TABLE 4—EFFECT OF Mn(II) IONS ON THE RATE OF OXIDATION OF PHENACYL BROMIDE

$[CrO_3]=0.001\ M$, [*m*-Nitro phenacyl bromide]=0.01 *M*, $[HClO_4]=0.4\ M$, Solvent=90% Acetic acid (v/v), Temp.=35°

$[Mn(II)]\times10^4\ M$	$k_1\times10^5\ sec^{-1}$
—	17.28
10	3.50
15	2.25
20	1.80
25	0.90

by Westheimer and Watanabe[14] for isopropanol oxidation. This is probably due to the Mn(II) catalysed disproportionation of intermediate valence states of [Cr(IV)]. It may be reasonable to propose the following reaction in the presence of Mn(II) ions.

$$3Cr(IV)+Mn(II) \longrightarrow Cr(V)+2Cr(III)+Mn(III)$$

Effect of complexing agent on reaction rate : The rate of the reaction decreases in the presence of certain dibasic acids and organic bases (Table 5). This may be due to complex forming ability of intermediate stages of the oxidant.

Effect of substituents on rate : The effect of substituents on the benzene ring of phenacyl bromide shows that electron donating groups enhance the reaction rate while electron withdrawing groups retard it (Table 6). The order of reactivity of different substituents is $p\text{-}OCH_3 > p\text{-}CH_3 > H > m\text{-}NO_2 > p\text{-}NO_2$. The log k_1 values for different substituted phenacyl bromides have been plotted against Brown's σ^+ values[15]. The value of ρ^+ was computed to be −0.20.

TABLE 5—EFFECT OF ADDED COMPLEXING AGENTS ON THE REACTION RATE

$[CrO_3]=0\ 001\ M$, [*m*-Nitro phenacyl bromide]=0.01 *M*, $[HClO_4]=0\ 4\ M$, Solvent—90% Acetic acid (v/v), [Complexing agent] 0 01 *M*, Temp. 35°

Complexing agent	$k_1\times10^5\ sec^{-1}$
Nil	17.28
Succinic acid	5.60
Adipic acid	4.50
Piperidine	5.05
Pyridine	4.02
Diethylamine	3.80

TABLE 6—REACTION RATES AND ARRHENIUS PARAMETERS FOR CHROMIC ACID OXIDATION OF SUBSTITUTED PHENACYL BROMIDES

$[CrO_3]$ 0 001 *M*, [Substrate]—0.01 *M*, $[HClO_4]=0.2\ M$, $\mu=1\ M$, Solvent—90% Acetic acid (v/v)

Substituent	$k\times10^5\ sec^{-1}$ at °C			E	$-\Delta S^*$
	30	35	40	k.cal/mole	e.u.
p-OCH_3	9.21	13.05	17 25	11.25	40.89
p-CH_3	8.20	12.02	16.15	12.46	38.08
H	7.60	10 80	13.55	13.12	36.03
m-nitro	5.44	8.82	12.80	15.36	33.59
p-nitro	4 44	7.75	10.85	17.06	24.04

Isokinetic relationship · A linear relationship between the entropy of activation (ΔS^*) and the enthalpy of activation (ΔH^*) has been observed for the oxidation[16]. The data can be fitted in the equation,

$$\Delta H^*=\Delta H_0^*+\beta\Delta S^*$$

ΔH_0 has the value 25.5 kcal mole^{-1} and β, the isokinetic temperature, is 381K for the reaction. The linear relationship shown by the majority of phenacyl bromides indicates that apparently the same mechanism prevails in all cases[17].

Discussion

The aliphatic haloketones undergo hydrolysis in acid and alkaline medium. But phenacyl bromides are found to resist hydrolysis even upto an acid concentration of 0.9 *M* $HClO_4$.

The oxidation of phenacyl bromides by H_2CrO_4 shows that, (i) the oxidation rate is first order with respect to the haloketone, (ii) the rate at which Cr(VI) disappears also follows first order rate laws, (iii) the reaction is acid catalysed and (iv) the value of ρ^+ is negative showing that electron donating groups enhance the reaction rate. The value of ΔS^* is negative indicating a rigid transition state.

The formation of free radicals was not indicated in the present investigation since polymerization with acrylonitrile or reduction of $HgCl_2$ could not be observed. Therefore the oxidation reaction is believed to proceed through an ionic intermediate.

As pointed out by Best *et al*[2], the rate of chromic acid oxidation of cyclohexanone by chromic acid is slower than its rate of enolization at the same acidity. Thus one cannot say whether the ketone molecule or its enol form is being attacked by the chromic acid. However, Rocek and Riche[3] have advanced different views which contradict the views suggested by Best *et al*[2]. The latter workers observed that the rate of oxidation is close to the enolization as determined by bromination measurement, demonstrating that the oxidation of ketones proceeds through the enol intermediate. Nayak *et al*[18] have studied the bromination of a large number of acetophenones. The present experimental condition is very much close to the bromination experiment. Various substituents change the rate in the same direction in both the reactions as evidenced by the magnitude and size of the Hammett ρ value. Thus it seems likely that the oxidation proceeds through an enol intermediate. This receives support from the DMSO oxidation of phenacyl bromide[19] and SeO_2 oxidation of a number of ketones[20].

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Synthesis of Some 3-Arylimino-5-(N-Methylanilino-)-1,2,4-Δ^4-Dithiazolines

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Some new 3-arylimino-5-(N-methylanilino)-1,2,4-Δ^4-dithiazolines have been synthesised by the oxidative debenzylation and cyclisation of the corresponding 5-aryl-1,1-methylphenyl-2-S-benzyliso-4-thiobiurets. The characterisation of these compounds have been achieved by the direct oxidation of the corresponding 2,4-dithiobiurets and also by infrared spectra.

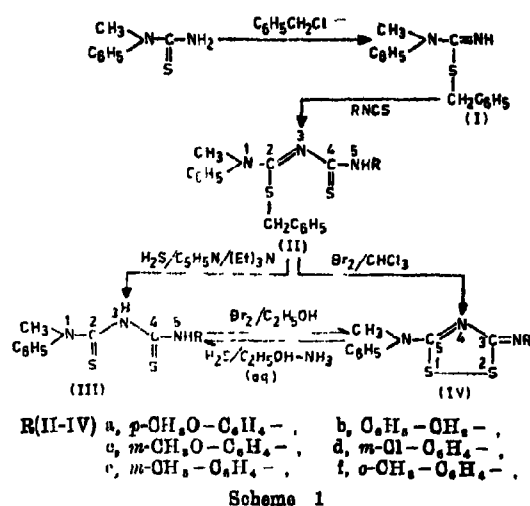
OXIDATION of 2,4-dithiobiurets has been a well studied method[1-5] for the synthesis of the related 1,2,4-dithiazolines/dithiazolidines. In the recent past we reported that substituted 1,2,4-dithiazolines/dithiazolidines could also be synthesised by the oxidative dealkylation of the related isodithiobiurets[6-10]. In the light of these observations, it was considered of interest to explore the potentiality of oxidative debezylation and cyclisation reaction for the synthesis of certain hitherto unreported 3-arylimino-5-(N-methylanilino-)-1,2,4-Δ^4-dithiazolines.

The present communication describes the synthesis of certain new 3-arylimino-5-(N-methylanilino-)-1,2,4-Δ^4-dithiazolines by the oxidative debenzylation and simultaneous ring closure of the corresponding 5-aryl-1,1-methylphenyl-2-S-benzyliso-4-thiobiurets.

N-Methylphenyl thiourea was benzylated with benzyl chloride. The expected 1,1-methylphenyl-2-S-benzylisothiourea free base (I) thus obtained was condensed with the appropriate arylisothiocyanate to yield the desired 5-aryl-1,1-methylphenyl-2-S-benzyliso-4-thiobiurets (II). These isodithiobiurets (II), on oxidation with molecular bromine in chloroform, gave the related 3-arylimino-5-(N-methylanilino-)-1,2,4-Δ^4-dithiazolines (IV). These have also been obtained by the direct oxidation of the related 5-aryl-1,1-methylphenyl-2,4-dithiobiurets (III) Compounds (III) were obtained by the reductive debenzylation of the corresponding isodithiobiurets (II) with dry hydrogen sulphide in pyridine-triethylamine medium and also by the reduction of the related dithiazolines (IV) with ethanolic ammoniacal hydrogen sulphide.

In all the cases the structure of the compounds (III) and (IV) were confirmed by their synthesis through alternative route as described above and also by mixed melting point, elemental analysis and identical ir spectra. The scheme of the reaction can be represented as follows.

R(II-IV) a, p-$CH_3O-C_6H_4-$, b, $C_6H_5-CH_2-$, c, m-$CH_3O-C_6H_4-$, d, m-$Cl-C_6H_4-$, e, m-$CH_3-C_6H_4-$, f, o-$CH_3-C_6H_4-$,

Scheme 1

Experimental

Melting points of the compounds are recorded on Kofler hot stage apparatus and are uncorrected. Infrared spectra were recorded in Nujol on Perkin-Elmer spectrophotometer, Model-720. N-Methylphenyl thiourea was prepared according to known procedure[11] and its S-benzyl derivative (I) was obtained by benzylation[12] with benzyl chloride.

5-Aryl-1,1-methylphenyl-2-S-benzyliso-4-thiobiurets (II) : The details of a typical experiment is as follows. The 1,1-methylphenyl-2-S-benzylisothiourea, m.p. 70° (5.0 g ; 0.019 mole) was refluxed with m-methoxyphenyl isothiocyanate (3.21 g ; 0.019 mole) in dry benzene for 4 hr on a water bath. The excess of benzene was evaporated and the semi-solid product, on washing with petroleum ether and treatment with a little ethanol, afforded 5-m-methoxyphenyl-1,1-methylphenyl-2-S-benzyliso-4-thiobiuret as a crystalline product. It was recrystallised from ethanol, m.p. 90°, yield 6.16 g (75%). The results of such experiments are summarised in Table 1.

TABLE 1—PHYSICAL DATA OF 5-ARYL-1,1-METHYLPHENYL-2-S-BENZYLISO-4-THIOBIURETS II (a-f)

Compound	Molecular formula	m.p. °C	Yield %	Analysis % Calcd. C	H	Found C	H
IIa	$C_{23}H_{23}N_3OS_2$	138	75	65.55	5.46	65.90	5.50
IIb	$C_{23}H_{23}N_3S_2$	127	74	68.14	5.67	68.30	5.71
IIc	$C_{23}H_{23}N_3OS_2$	90	75	65.55	5.46	65.80	5.53
IId	$C_{22}H_{20}ClN_3S_2$	118	69	62 04	4.70	62.23	4.91
IIe	$C_{23}H_{23}N_3S_2$	122	64	68.14	5.67	68.21	5.71
IIf	$C_{23}H_{23}N_3S_2$	88	50	68.14	5.67	68.20	5.73

Typical IR frequencies (cm^{-1}) of 5-*m*-methoxyphenyl-1,1-methylphenyl-2-S-benzyliso-4-thiobiuret, 3200m NH stretching (lit. 3400-3100)[13], 1125m, 1140vs, 1200w N–C(=S)–N grouping (lit. 1100-1200)[14a], 1600w N–C=N grouping (lit. 1686-1582)[14b].

3-Arylimino-5-(N-methylanilino-)-1,2,4-Δ^4-dithiazolines (IV) :

(i) *Oxidative debenzylation of 5-aryl-1,1-methylphenyl-2-S-benzyliso-4-thiobiurets :* The experimental details of a typical experiment follows: The 5-*m*-methoxyphenyl-1,1-methylphenyl-2-S-benzyliso-4-thiobiuret (2 g), made into a paste with chloroform, was treated with molecular bromine with vigorous stirring until the colour of bromine persisted. The reaction mixture warmed up appreciably evolving lachrymatory fumes of benzyl bromide. After 1 hr the semi-solid product was first washed with ether and the addition of a little ethanol thereafter gave the hydrobromide of the oxidation product which separated out as a crystalline product. On treatment with aqueous ammonia 3-*m*-methoxyphenylimino-5-(N-methylanilino-)-1,2,4-Δ^4-dithiazoline was obtained, which was thoroughly washed with ether and crystallised from ethanol, m.p. 168°, yield 1.06 g (68%).

The dithiazoline bases so obtained showed no depression in m.p. when mixed with authentic samples obtained by the oxidation of the corresponding 1,1,5-trisubstituted-2,4-dithiobiurets (Table 2).

TABLE 2—PHYSICAL DATA OF 3-ARYLIMINO-5-(N-METHYLANILINO-)-1,2,4-Δ^4-DITHIAZOLINES IV (a-f)

Compound	Molecular formula	m p. °C	Yield %	Analysis% Calcd. C	H	Found C	H
IVa	$C_{16}H_{15}N_3OS_2$	110	78	58.35	4.55	58 61	4.49
IVb	$C_{16}H_{15}N_3S_2$	94	71	61.34	4.79	61.54	4.83
IVc	$C_{16}H_{15}N_3OS_2$	168	68	58.35	4.55	58.63	4 56
IVd	$C_{15}H_{12}ClN_3S_2$	85	70	53 97	3.59	54.02	3.71
IVe	$C_{16}H_{15}N_3S_2$	110	72	61.34	4.79	61.79	4.82
IVf	$C_{16}H_{15}N_3S_2$	125	60	61.34	4 79	61.80	4.79

Typical IR frequencies (cm^{-1}) of 3-*m*-methoxyphenylimino-5-(N-methylanilino-)1,2,4-Δ^4-dithiazoline, C=N 1625[13], ring S-S-linkage 488s[15], the absence of IR band for N–H is remarkable.

(ii) *Oxidation of 5-aryl-1,1-methylphenyl-2,4-dithiobiurets* (III) *with bromine in ethanol :* 5-*m*-Methoxyphenyl-1,1-methylphenyl-2,4-dithiobiuret (2 g), listed in Table 3, was oxidised with bromine in ethanolic solution. The excess of ethanol was evaporated and the resultant mass washed with ether when hydrobromide of the 3-*m*-methoxyphenylimino-5-(N-methylanilino-)-1,2,4-Δ^4-dithiazoline was obtained. The free base was obtained by the treatment of the hydrobromide with aqueous ammonia and it was crystallised from ethanol, m.p. 168°, yield 1.5 (80%) (Table 2).

5-Aryl-1,1-methylphenyl-2,4-dithiobiurets (III) :

(i) *Reductive debenzylation of 5-aryl-1,1-methylphenyl-2-S-benzyliso-4-thiobiurets* (II) *with hydrogen sulphide in pyridine-triethylamine medium :* Through a solution of 5-*m*-methoxyphenyl-1,1-methylphenyl-2-S-benzyliso-4-thiobiuret (5 g) in pyridine (50 ml) and triethylamine (6 ml), a stream of dry hydrogen sulphide was passed for 4 hr. The reddish brown viscous liquid so obtained was poured over crushed ice, acidified with dilute hydrochloric acid and diluted with water. On standing for about 1 hr, 5-*m*-methoxyphenyl-1,1-methylphenyl-2,4-dithiobiuret was obtained as a granular solid. Purification was effected by dissolving the product in dilute aqueous sodium hydroxide solution and reprecipitation with hydrochloric acid followed by crystallisation from ethanol, m.p. 132°, yield 61% (Table 3).

TABLE 3—PHYSICAL DATA OF 5-ARYL-1,1-METHYLPHENYL-2,4-DITHIOBIURETS III (a-f)

Compound	Molecular formula	m.p °C	Yield %	Analysis% Calcd C	H	Found C	H
IIIa	$C_{16}H_{17}N_3OS_2$	160	69	58.00	5.13	58.13	5 39
IIIb	$C_{16}H_{17}N_3S_2$	169	63	60 95	5 39	61.10	5.43
IIIc	$C_{16}H_{17}N_3OS_2$	132	61	58 00	5 13	58 29	5 17
IIId	$C_{15}H_{14}ClN_3S_2$	102	59	53 65	4.17	53.71	4.19
IIIe	$C_{16}H_{17}N_3S_2$	110	58	60 95	5 39	61.09	5 25
IIIf	$C_{16}H_{17}N_3S_2$	98	60	60.95	5.39	61.21	5.41

Typical IR frequencies (cm^{-1}) of 5-*m*-methoxyphenyl-1,1-methylphenyl-2,4-dithiobiurets, 3385w NH-stretching[13], 1155m N–C(=S)–N–grouping[14a].

(ii) *Reduction of 3-arylimino-5-(N-methylanilino-) 1,2,4-Δ^4-dithiazolines with ethanolic ammoniacal hydrogen sulphide :* 3-*m*-Methoxyphenylimino-5-(N-methylanilino-)-1,2,4-Δ^4-dithiazolines (4 g) was dissolved in hot ethanolic ammoniacal hydrogen sulphide solution and a stream of hydrogen sulphide passed for 3 hr. The clear solution thus obtained on dilution with water or acidification with dilute hydrochloric acid afforded 5-*m*-methoxyphenyl-1,1-methylphenyl-2,4-dithiobiuret. It was crystallised from ethanol, m.p. 132°, yield 61% (Table 3).

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Preparation, Synthesis and Mass Spectral Studies of 3-(*p*-Nitrophenyl)-thiazolo-[2,3,c][1,2,4]-triazepine Derivatives

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Preparation of 3-(p-nitrophenyl)-thiazolo[2,3,-c][1,2,4-] triazepine derivatives (I, II and III) through the condensation of 2-hydrazino-4-(p-nitrophenyl)-thiazole with ω-benzoyl acetophenone, acetylacetone and ethylacetoacetate and their mass spectral analysis is reported.

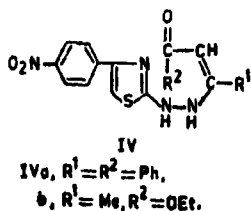
THE importance and extensive use of seven membered heterocyclic compounds like Serax and Megadon[1] as psychosedative and tranquilising agents prompted us to prepare similar seven membered ring system fused to thiazole nucleus and we have prepared the following three compounds, I, II and III.

I II III

Condensation of 2-hydrozino-4-(*p*-nitrophenyl)-thiazole[2], prepared from 2-chloro-4-(*p*-nitrophenyl)-thiazole, with ω-benzoyl acetophenone, acetyl acetone and ethylacetoacetate gave I, II and III, respectively. The intermediates (IV) were also isolated from the reactions. All attempts for cyclisation of the intermediate failed, even after prolonged heating with glacial acetic acid.

IV

IVa, $R^1=R^2=Ph$,

b, $R^1=Me, R^2=OEt$.

IR spectrum of IVb showed absorption at 1725 cm^{-1} (CO_2Et) while that of III showed a band at 1640 cm^{-1} (>C=O). IR spectrum of IVa showed absorption at 1640 cm^{-1} ($-\overset{O}{\overset{\|}{C}}-C_6H_5$) while that of I and II showed the absence of this band. The mass spectra of I-III confirmed their structure.

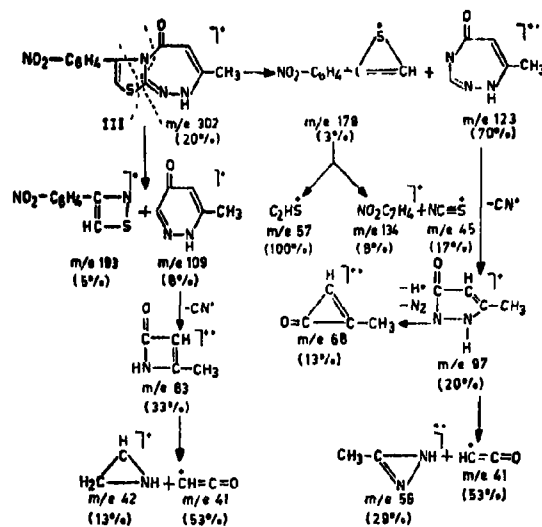



Chart 1

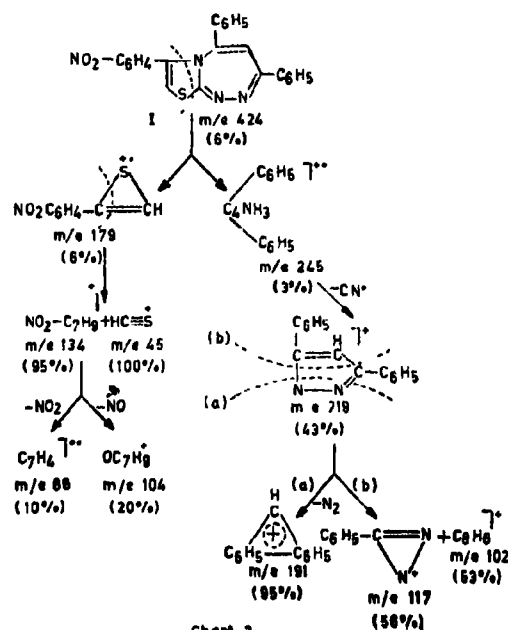



Chart 2

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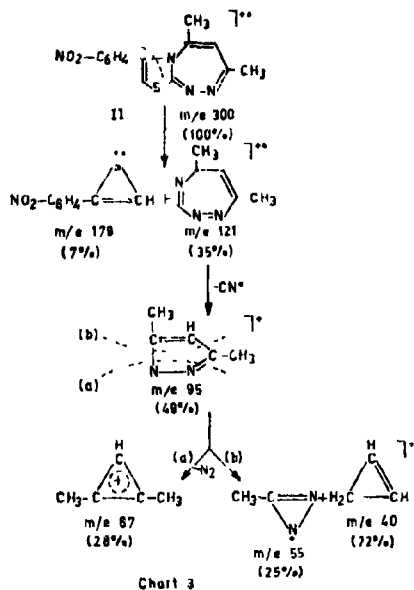
TABLE 1

Compound	Crystallising solvent	Molecular formula	m.p °C	Yield %	Analysis% Found (Calcd.) C	H	N	S
I	Chloroform-Pet. ether	$C_{24}H_{16}N_4O_2S$	240	50	67.89 (67 92)	3.76 (3.77)	13.01 (13.20)	7.53 (7.54)
II	Pet. ether	$C_{17}H_{12}N_4O_2S$	196 200	70	55.98 (56.0)	4 34 (4.33)	18.65 (18.66)	10.60 (10.66)
III	Ethanol	$C_{13}H_{10}N_4O_3S$	220-21	60	51.60 (51.65)	3.29 (3 31)	18.50 (18.54)	10.56 (10.50)
IVa	Ethanol	$C_{24}H_{18}N_4O_3S$	228-30	40	65.05 (65.15)	4.01 (4 07)	10.36 (10.40)	7.20 (7.23)
IVb	Ethanol	$C_{15}H_{16}N_4O_4S$	235-37	40	51.70 (51.72)	4.32 (4.31)	16.0 (16.09)	9 89 (9.91)

Chart 3

The melting points are uncorrected. The purity of the compounds were routinely checked by tlc. IR spectra were recorded in KBr on a Perkin-Elmer Infrared spectrophotometer. Mass spectra were determined on a Varian Mat CH – 7 instrument at 70 e.v. using direct inlet.

*General procedure for the synthesis of 3-(*p*-nitrophenyl)-thiazole-[2,3-*c*][1,2,4]-triazepine derivatives (I-III)* : A mixture of 2-hydrazino-4-(*p*-nitrophenyl)-thiazole (2.36 g ; 0.01 mole), ω-benzoylacetophenone/acetylacetone/ethylacetoacetate (0.01 mole) and glacial acetic acid (10-35 ml) was heated under reflux for 2 hr. The solid obtained on cooling was filtered, washed and dried. The intermediate products (IV) were isolated by fractional crystallisation of this solid with suitable solvents. All the compounds (I-IV) were purified by repeated crystallisation (Table 1).

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Studies on Heterocyclic Compounds. Part—V : Synthesis and Antimicrobial Activities of N-Bridged Thiazole and Imidazole Derivatives

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Several benzoxazolo[3,2-b]thiazolium, benzothiazolo[3,2-b]thiazolium and pyridino[2,1-b]thiazolium perchlorate salts, thiazolo[3,2-a]pyrimidine and several of their higher homologues as hydrobromides (IV) and free bases, were synthesised by reacting the respective mercapto compounds with α-bromoketones The free bases as well as the hydrobromides of 1,3,4-thiadiazolo[3,2-b]imidazoles (VI) and 1,3,4-oxadiazolo[3,2-b]imidazoles (VII) were synthesised by the reaction of aminoazoles with the same bromoketones. Besides these, the synthesis of a few reduced N-bridged thiazole compounds (V) prepared by reacting the mercapto compounds with dihaloalkanes has been described. The structures of these compounds have been confirmed from spectral and analytical data and their bactericidal and fungicidal potencies have been evaluated.

THE versatile use of thiazole and imidazole compounds possessing -N-C-S-, -N-C-N- grouping respectively as antitubercular[1] and antiradiation[2] agents and their applications as anthelmintics[3], nematocides[4] and vulcanisation accelerators[5] have stimulated considerable interest to explore the possible synthesis of new potential compounds in which the thiazole or imidazole ring is fused with another biologically active nucleus through nitrogen atom. In the present communication, the synthesis of three types of such N-bridged thiazole derivatives in which the thiazole ring is fused to another heterocyclic ring such as benzothiazole, benzoxazole, pyridine, reduced pyrimidine and its higher homologues, imidazoline, thiadiazole and oxadiazole has been reported.

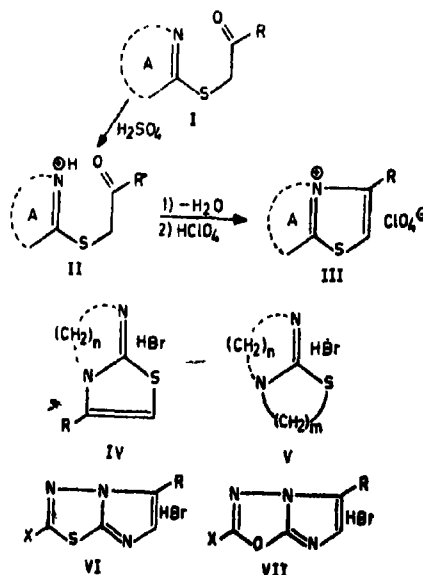
The N-bridged compounds (III), isolated as perchlorate salts were obtained by reacting the sodium salt of the mercapto compounds with α-bromoketones. The ketosulphides (I), isolated as intermediates, were cyclised in the presence of conc H_2SO_4. The uv spectrum of the ketosulphide (I ; A = benzothiazolyl-2, R = phenyl) showed a broad band at 290 nm correspondingly to $\pi \rightarrow \pi^*$ transition whereas its cyclised products (III) showed a bathochromic shift and the band appeared at 312 nm due to the extensive conjugation of the π bonds. Similarly the ir of the same ketosulphide gave a sharp carbonyl absorption at 1730 cm^{-1} which was absent in the cyclised product. The second type of N-bridged thiazolo compounds (IV), isolated as the hydrobromides, were prepared by reacting the cyclic thioureas with bromoketones by following the general procedure reported by Chadha *et al*[6,7]. The free bases of the hydrobromide salts have also been isolated after neutralising the aqueous solution either with K_2CO_3 or ammonia. The third type of fused thiazole derivatives (V) in which thiazole or thiazine moieties are partially saturated were synthesised by reacting the alkylhalides (1,2-dichloroethane, 1,3-dibromopropane and 1,4-dibromobutane) with a few cyclic thioureas.

Besides these, the N-bridged imidazole derivatives (VI and VII) in which the ring is fused with either 1,3,4-thiadiazolyl or 1,3,4-oxadiazolyl moiety have been synthesised by reacting the 2-amino-5-substituted thiadiazoles and oxadiazoles respectively with bromoketones.

I

II $\xrightarrow{1)\ -H_2O;\ 2)\ HClO_4}$ III

IV V

VI VII

Antimicrobial tests : The bactericidal activities of the compounds were evaluated by agar plate

technique using *S. aureus* and *B. subtilis* and fungicidal tests were carried out using *A. niger* and *C. albican* in Sabouraud's broth medium.

Experimental

All melting points are uncorrected. IR spectra of the compounds were taken on KBr disc in Perkin-Elmer 293 spectrophotometer.

Benzoxazolyl-2-phenacyl sulphide (I ; *A*=*benzoxazolyl-2, R*=C_6H_5) : 2-Mercaptobenzoxazole (3 g, 0.02 mole) in methanol (70 ml) was taken in a 500 ml round bottomed flask provided with a mechanical stirrer. Metallic sodium (0.02 mole) was added to it protion wise. To the resulting clear solution phenacylbromide (2.0 g) was added in portions with stirring and the mixture was allowed to stand at room temperature overnight The needle-shaped crystals were filtered off, m.p. 115-116°, yield 2.0 g (70%). (Found : S, 12.90. $C_{15}H_{11}O_2NS$ requires S, 12.89%) ; λ_{max}^{EtOH} (nm) . 276 ($\epsilon = 5\times10^5$) ; ν_{max}^{KBr} (cm^{-1}) : 2845, 1750, 1690.

3-Phenylbenzoxazolo [3,2-b]thiazoliumperchlorate (III ; *A*=*benzoxazolyl-2, R* C_6H_5) · The above ketosulphide (1.35 g) was dissolved in ice cold conc H_2SO_4 (12 ml) and the mixture was allowed to stand at room temperature for 24 hr. The resulting solution was then poured cautiously to 300 ml of ice cold anhydrous ether and the mixture was kept in the refrigerator for 2 days. The ether layer was decanted off from an oil The ether was evaporated at room temperature and the residue was dissolved in small quantity of water and filtered. The solution was treated with 35% $HClO_4$ (5 ml) and kept overnight during which the perchlorate salt precipitated out. It was filtered, washed several times with cold ether and dried in air, m.p. 202-3°, yield 62%. (Found : S, 8.85. $C_{15}H_{10}NO_5SCl$ requires 9.10%) ; λ_{max}^{EtOH} (nm) : 307 ($\epsilon = 4\times10^6$) ; ν_{max}^{KBr} (cm^{-1}) 1685, 1206.

Benzothiazolyl-2-phenacyl sulphide (I : *A*-*benzothiazolyl-2, R*-C_6H_5) : This was prepared as colourless needles by taking 2-mercaptobenzothiazole (0.42 g), metallic sodium (0.05 g) and phenacylbromide (0.5 g) in methanol (20 ml) by following the above procedure, m.p. 207°, yield 350 mg (50%). (Found : S,22.18. $C_{15}H_{11}NS_2O$ requires S, 22.45%); λ_{max}^{EtOH} (nm) : 290 (ϵ – 3.2×10^4) ; ν_{max}^{KBr} (cm^{-1}) : 2910, 1750, 1685, 1305.

3-Phenylbenzothiazolo[3,2-b]thiazolium perchlorate (III ; *A*=*benzothiazolyl-2, R*=C_6H_5) : The above ketosulphide (0.28 g) was cyclised with ice cold conc H_2SO_4 (5 ml) and the product was isolated as perchlorate salt by following the general work up procedure, m p. 221°, yield 50%. (Found : S, 17.19. $C_{15}H_{10}O_4NS_2Cl$ requires S, 17.42%) ; λ_{max}^{EtOH} (nm) : 310 ($\epsilon = 6\times10^5$) ; ν_{max}^{KBr} (cm^{-1}) : 1690 1460, 1300.

Pyridyl-2-phenacyl sulphide (I ; *A*=*pyridyl-2, R*=C_6H_5) : This was prepared from 2-mercaptopyridine (1.1 g) and phenacylbromide (2.0 g) in methanol and metallic sodium (0.2 g) by following the general procedure as colourless needles, m.p. 107°, yield 1.4 g (65%). (Found : S, 13.97. $C_{13}H_{11}NSO$ requires S, 13.84%).

3-Phenyl-pyridino[2,1-b]thiazolium perchlorate (III ; *A*-*pyridyl-2, R*=C_6H_5) · The above thioketone (1.15 g) was cyclised using conc H_2SO_4 and the product was isolated as the perchlorate salt, m p 207°(d). (Found S, 14.02. $C_{13}H_{11}NOS$ requires S, 13.97%).

3-Phenyl-4,5,6,7,-tetrahydrothiazolo[3,2-a]pyrimidine hydrobromide (IV ; *N*=*3, R*-C_6H_5) : A mixture of 2-mercapto-3,4,5,6-tetrahydropyrimidine (1.16 g ; 0.01 mole) and phenacylbromide (2 g) in ethanol (25 ml) was heated under reflux on a water bath for 12 hr. Dirty white crystals separated after concentrating the solution. It was filtered and recrystallised from ethanol as white crystals, m p. 258°, yield 2.1 g (70%). (Found : S, 10.75 ; Br, 26.62 $C_{12}H_{13}N_2SBr$ requires S, 10.77 ; Br, 26.93%).

The free base was obtained after neutralising the aqueous solution with K_2CO_3 in almost quantitative yield, m.p. 139°. (Found · S, 14.43. $C_{12}H_{12}N_2S$ requires S, 14.81%)

3-Phenyl-5,6,7,8-tetrahydrothiazolo[3,2-a](1, 3) diazepine hydrobromide (IV ; *n* -*4, R* · C_6H_5) : It was prepared by taking 2-mercaptodiazepine (1.30 g ; 0.01 mole) and phenacylbromide (2 g) in ethanol (20 ml) following the general work up procedure mentioned earlier, m p. 246°, yield 1.2 g (35%). (Found · S,11.80. $C_{13}H_{15}N_2SBr$ requires S,10.29%).

The free base was obtained as crystalline needles after neutralisation with aqueous ammonia, m.p. 111 . (Found S, 13.63. $C_{13}H_{14}N_2SBr$ requires S, 13.91%).

2,3,5,6-Tetrahydrothiazolo[3,2-a]imidazole hydrochloride (V ; *n* · *m*=*2*) Ethylene thiourea (0.4 g) and 1,2-dichloroethane (0.4 g) in absolute alcohol (20 ml) were refluxed on a water bath for 6 hr. After cooling, fine crystals of thiazoloimidazole hydrochloride separated, m.p. 196°, yield 0.5 g (63%). (Found : S, 19.04. $C_5H_9N_2SCl$ requires S, 19.45%).

The other compounds prepared by the above procedure are V (n=3, m=2, X -Cl), m.p. 206°. (Found . S, 17.86. $C_6H_{11}N_2SCl$ requires S, 18.13%) ; V (n=4, m=2, X=Cl), m.p. 217°. (Found : S, 17.54. $C_7H_{13}N_2SCl$ requires S, 17.68%) : V (n=2, m=4, X=Br), m.p. 208(d). (Found : S, 13.44. $C_7H_{13}H_2SBr$ requires S, 13.67%) ; V (n=m=3, X=Br), m.p. 214°. (Found : S, 13.51. $C_7H_{13}N_2SBr$ requires S, 13.67%).

2,5-Diphenyl-1,3,4-oxadiazolo[3,2-b]imidazole hydrobromide (VII ; *X*=*R*=C_6H_5) · A mixture of 2-amino-5-phenyl oxadiazole (0.16 g) and phenacylbromide (0.2 g) in alcohol (15 ml) was heated under reflux on a water bath for 6 hr. The colourless solid separated after cooling was filtered,

Table 1—Analytical Data and Test Results of Perchlorate Salts (III)

A	R	m.p. °C	%S Found (Calcd.)	SA	BS	CA*	AN*
Benzoxazolyl-2	Phenyl	—	—	+	+	50	50
—do—	p-Chlorophenyl	223	8.15 (8.29)	+	2+	50	50
—do—	p-Anisyl	246	8.21 (8.38)	+	+	–	–
—do—	Thienyl-2	214	18.61 (18.74)	2+	+	100	100
—do—	Furyl-2	197	9.70 (9.88)	+	+	—	–
Benzothiazolyl-2	Phenyl	—	—	2+	2+	50	50
—do—	p-Chlorophenyl	226	15.65 (15.92)	2+	2+	100	100
—do—	p-Anisyl	218	16.06 (16.10)	+	–	–	–
—do—	Thienyl-2	205	26.78 (26.85)	2+	+	–	100
—do—	Furyl-2	187	9.25 (9 37)	+	–	–	–
Pyridyl-2	Phenyl	—	—	+	–	–	–
—do—	Thienyl-2	176	20.00 (20.15)	+	+	–	100
—do—	Furyl-2	144	10.29 (10.61)	–	–	–	–

SA = *S. aureus*, BS = *B. subtilis*, CA = *C. albican*, AN = *A. niger*, + = zone size 6-8 mm, 2+ = zone size 9-14 mm, – = inactive.
*The number indicates minimum inhibitory concentration in μg/ml.

Table 2

n	R	Hydrobromide (IV) m p °C	%Br Found (Calcd.)	SA	BS	CA*	AN*	Free base m.p. °C	%S Found (Calcd)
3	Phenyl		—	–	+	100	—	—	—
	p-Chlorophenyl	250	—	+	–	—	—	150	12.42 (12.74)
	Thienyl-2	236	26.15 (26.40)	+	2+	50	50	144	28.56 (28.82)
	Furyl-2	235	27 64 (27.87)	+	+	—	—	123	15.34 (15.53)
	p-Nitrophenyl	250	—	+	–	—	—	165	11.70 (11.98)
4	Phenyl	246	—	+	+	100	—	—	—
	p-Chlorophenyl	213	—	+	2+	100	—	120	11.68 (12.07)
	Thienyl-2	176	25.16 (25.23)	2+	–	—	100	164	27.16 (27.11)
	Furyl-2	189	26 30 (26.57)	+	–	—	—	150	—
	p-Nitrophenyl	193	—	–	–	—	—	129	11.25 (11.38)
5	Phenyl	213	22.24 (24.61)	+	–	—	—	130	13.10 (13.11)
	p-Chlorophenyl	212	—	+	+	—	—	146	12.23 (12.35)
6	Phenyl	209	24.46 (24.31)	+	–	—	—	117	12.29 (12.40)
7	Phenyl	200	23 10 (23.32)	+	+	—	—	106	—
8	Phenyl	207	22.24 (22.40)	+	+	—	—	111	11.12 (11.18)

SA = *S. aureus*, BS = *B. subtilis*, CA = *C. albican*, AN = *A. niger*, + = zone size 6-8 mm, 2+ = zone size 9-14 mm, – = inactive
*The number indicates minimum inhibitory concentration in μg/ml.

washed with ether and dried, m.p. 226°, yield 150 mg (70%). (Found : Br, 23.18. $C_{16}H_{18}N_3OBr$ requires Br, 23.32%).

The above hydrobromide was dissolved in water and neutralised by conc NH_4OH during which the free base separated in quantitative yield. It was

TABLE—3

X	R	Hydrobromide (VI) m.p. °C	%Br Found (Calcd.)	SA	BS	CA**	AN**	Free base m.p. °C	%S Found (Calcd.)	BS
H	Phenyl	235	28.48 (28.27)	2+	–	–	–	198	15.52 (15.76)	+
—do—	p-Chlorophenyl	238	–	2+	–	–	–	193	13.45 (13.53)	–
Phenyl	Phenyl	254	22 72 (22.88)	–	–	100	–	192	11.32 (11.52)	–
—do—	p-Chlorophenyl	237	–	–	+	–	–	172	—	–
p-Anisyl	Phenyl	218	20 48 (20 57)	2+	+	50	–	252	10.09 (10.23)	+
—do—	p-Chlorophenyl	285	—	–	–	–	–	244	9.18 (9.22)	–
p-Chlorophenyl	Phenyl	250	20.13 (20.38)	+	+	50	–	216	10.28 (10.39)	+
—do—	p-Chlorophenyl	250	—	–	–	50	–	282	—	+
Hydrobromides (VII)										
Phenyl	Phenyl	225	23 18 (23.82)	+	+	–	–	208	15.76* (16.03)	+
—do—	p-Chlorophenyl	222	—	–	–	–	–	198	—	–
p-Chlorophenyl	Phenyl	231	21.12 (21.19)	–	+	–	–	142	—	–
—do—	p-Chlorophenyl	227	—	–	–	–	–	118	12.46* (12.65)	–
p-Anisyl	Phenyl	220	21.28 (21.45)	–	–	100	–	238	–	+
—do—	p-Chlorophenyl	234	—	–	–	–	–	234	–	–

* indicates estimated sulphur percentage.

filtered, washed with water and recrystallised from ethanol, m p. 208°. (Found : N, 15.78. $C_{16}H_{12}N_3O$ requires N, 16.03%).

3-Phenyl-(1,3,4-thiadiazolo)[3,2-b]imidazole hydrobromide (VI ; $X=H$, $R=C_6H_5$) : It was obtained as crystalline needles from 2-aminothiadiazole (0.5 g) and phenacylbromide (0.5 g) by following the above procedure, m.p. 235°, yield 400 mg (60%). (Found · Br, 28.30. $C_{10}H_8N_3Br$ requires Br, 28.27%).

The free base was obtained after neutralisation with ammonia as pale yellow solid, m.p. 198°, yield 58%. (Found : S, 15.52. $C_{10}H_7N_3S$ requires S, 15.76%).

The physical and analytical data and antimicrobial test results of various perchlorate salts, thiazolopyrimidine and their higher homologues and thiazolo thiaoxadiazolo derivatives have been presented in Tables 1, 2 and 3, respectively.

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Synthesis of 3-(*p*-Fluoro)benzoylhydrazono-5-substituted-2-indolinones as Potential Biologically Active Agents†

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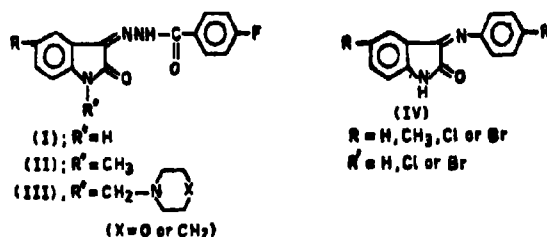
Different 5-substituted isatins have been condensed with *p*-fluoro benzoic acid hydrazide to furnish 3-(*p*-fluoro)benzoylhydrazono-5-substituted-2-indolinones (I). Similarly, reaction of N methyl-5-substituted isatins with *p*-fluorobenzoic acid hydrazide yielded 1-methyl-3-(*p*-fluoro)benzoylhydrozono-5-substituted-2-indolinones (II). When I were subjected to Mannich reaction 1-aminomethyl-3-(*p* fluoro)benzoylhydrazono-5-substituted-2-indolinones (III) were obtained. These compounds were screened for antibacterial activity against *B. megaterium*, *X. malvacearum*, *E. coli* and *B. subtilis* as well as for CNS activity.

ISATINS are known for their antiviral[1], antibacterial[2,3], anthelmintic[4] and herbicidal[5] properties. In addition, cysticidal[6], hypotensive responses and anticonvulsant activity[7] have also been reported in certain isatin derivatives. The antibacterial activity of different benzoic acid hydrazides is well established[8,9]. Certain organofluorine compounds have been reported as antibacterial[10,11] and CNS active agents[12,13]. In view of all these, it was considered of interest to synthesise certain fluorine containing acid hydrazide incorporated isatins and to evaluate them for their antibacterial activity and CNS activity.

For the synthesis of I, II and III, the starting materials, 5-substituted isatins, were prepared via Sandmeyer reaction[14]. *p*-Fluorobenzoic acid hydrazide was prepared from the methyl ester of *p*-fluoro benzoic acid and hydrazine hydrate. Condensation of various *p*-substituted isatins with *p*-fluorobenzoic acid hydrazide yielded 3-(*p*-fluoro)-benzoylhydrazono-5-substituted-2-indolinones (I). I were also prepared successfully by amine exchange reaction i.e., refluxing 5-substituted-3-arylimino-2-indolinones (IV) with *p*-fluorobenzoic acid hydrazide. Identity of both the products was checked by tlc, m.p., mixed m.p. and ir data. Mannich condensation on I, obtained via both the routes, yielded the same Mannich base which indicated that I prepared via both the route was the same. Treatment of 5-substituted isatins with dimethyl sulphate in ethanolic potassium hydroxide yielded N-methyl-5-substituted-2-indolinones, which on treatment with *p*-fluorobenzoic acid hydrazide yielded N-methyl-5-substituted-3-(*p*-fluoro)benzoylhydrazono-2-indolinones (II). Mannich condensation of I with amines furnished III. All the synthesised compounds gave satisfactory elemental analysis. Further support for their structures was derived from ir, nmr and mass spectral data. With a view to rule out the possibility of aminomethylation at –NH of benzoylhydrazono group in I during Mannich condensation, II (R = Cl) was heated with morpholine and formalin. In this reacton II was

(I); R' = H
(II); R' = CH_3
(III), R' = CH_2–N◯X
(X = O or CH_2)

(IV)
R = H, CH_3, Cl or Br
R' = H, Cl or Br

recovered unchanged and its identity was established on the basis of m.p., mixed m.p., ir and tlc.

Experimental

Melting points were taken in open capillaries and are uncorrected. IR spectra were taken in KBr and were as expected. NMR spectra were taken in $CDCl_3$ at 90 MHz. Mass spectra were recorded at 70 eV.

3-(p-Fluoro)benzoylhydrazono-5-substituted-2-indolinones (I) :

Method A : A mixture of isatin (4.4 g; 0.03 mole) and *p*-fluorobenzoic acid hydrazide (4.2 g; 0.03 mole) in ethanol (25 ml) was refluxed for 4 hr in presence of 2-3 drops of glacial acetic acid. The reaction mixture was then cooled to room temperature and the solid product was filtered and washed with ethanol (Table 1).

TABLE 1—3-(*p*-FLUORO)BENZOYLHYDRAZONO-5-SUBSTITUTED-2-INDOLINONES (I)

Sl. No.	R	Yield %	m.p. °C	Molecular formula
1.	H	78	>270	$C_{15}H_{10}FN_3O_2$
2.	CH_3	75	>260	$C_{16}H_{12}FN_3O_2$
3.	Cl	70	>260	$C_{15}H_9ClFN_3O_2$
4.	Br	82	>260	$C_{15}H_9BrFN_3O_2$

† Part XXXIII of the series Potential Biologically Active Agents.

TABLE 3—AMINOMETHYL-3-(*p*-FLUORO)BENZOYLHYDRAZONO-5-SUBSTITUTED-2-INDOLINONES (III)

Sl. No.	R	X	Yield %	m.p. (°C)	Molecular formula	Analysis% Calcd.	Found
9.	H	CH_2	62	268-269	$C_{21}H_{21}FN_4O_2$	N, 14.78	14 48
10.	H	O	65	207-208	$C_{20}H_{19}FN_4O_3$	C, 62.82	61.95
						H, 4.97	5.01
11.	CH_3	CH_2	68	195-196	$C_{22}H_{23}FN_4O_2$	C, 67.00	66.73
						H, 5.83	5.51
						N, 14 21	13.81
12.	CH_3	O	68	217-218	$C_{21}H_{21}FN_4O_3$	C, 63 68	62.98
						H, 5.30	5.13
13.	Cl	CH_2	62	190d	$C_{21}H_{20}ClFN_4O_2$	C, 60 79	60.95
						H, 4.82	5 45
14.	Cl	O	62	215	$C_{20}H_{18}ClFN_4O_3$	C, 57.62	57 80
						H, 4.32	4.25
						N, 13.44	13.16
15.	Br	CH_2	64	197-198	$C_{21}H_{20}BrFN_4O_2$	N, 12.20	12.20
16.	Br	O	68	213-214	$C_{20}H_{18}BrFN_4O_3$	C, 52.06	51.60
						H, 3.90	3.71
						N, 12.14	11.88

Mass spectra No. 11 – M^+, m/e 394
No. 16 – M^+, m/e 460/462

PMR (δ value) : 15, 1 42 (6H, $-CH_2CH_2-$), 2.26(4H, $N\langle^{CH_2}_{CH_2}$)
4.35 (2H, $N-CH_2N$), 6.80—7.40 (4H, $-C_6H_4-F$),
7.81 – 7.96 (3H, remaining Ar – H).

Method B : I were also prepared successfully by amine exchange reaction in which 3-arylimino group of 5-substituted-3-arylimino-2-indolinones was replaced by (*p*-fluoro)benzylhydrazono group. 5-Substituted-3-arylimino-2-indolinone (0.005 mole) was refluxed with *p*-fluoro benzoic acid hydrazide (0.005 mole) in ethanol (10 ml) for 6 hr. The solid obtained after cooling the reaction mixture was filtered, washed well with ethanol. Identity of I, prepared by method B, was checked by m.p., mixed m.p., tlc and ir spectral data. Identical Mannich bases (III) obtained from I, prepared by methods A and B, further established their identity.

N-Methyl-3-(p-fluoro)benzoylhydrazono-5-substituted-2-indolinones (II) : 5-Chloro-N-methyl-isatin (1.95 g ; 0.01 mole) was refluxed with *p*-fluorobenzoic acid hydrazide (1.55 g ; 0 01 mole) in ethanol (20 ml) for 4 hr in presence of 2-3 drops of glacial acetic acid. The reaction mixture was cooled to room temperature and the resultant product was filtered, washed well with ethanol and recrystallised from ethyl acetate (Table 2).

TABLE 2—N-METHYL-3-(*p*-FLUORO)BENZOYLHYDRAZONO-5-SUBSTITUTED-2-INDOLINONES (II)

Sl. No.	R	Yield %	m.p. °C	Molecular formula	Analysis% Calcd.	Found
5.	H	69	218-220	$C_{16}H_{12}FN_3O_2$	C, 64.64	64.21
					H, 4.04	3.89
6.	CH_3	75	206-207	$C_{17}H_{14}FN_3O_2$	N, 13.50	13.64
7.	Cl	72	203-204	$C_{16}H_{11}ClFN_3O_2$	C, 57.91	57.72
					H, 3.31	3 31
					N, 12.66	12.61
8.	Br	70	213-214	$C_{16}H_{11}BrFN_3O_2$	N, 11.17	10 84

Mass spectra ; No. 7 – M^+, m/e 381/383.

Reaction of II (*R-Cl*) *with morpholine and formalin :* II (0.005 mole) (R=Cl) was suspended in 10 ml of warm ethanol. Morpholine (1 ml) and formalin (1 ml) was added and the mixture stirred at 80° for 30 min. Working up the reaction mixture yielded a solid which was recrystallised from ethyl acetate. Its mixed m.p. with compounds 7 showed no depression. The product was identical with compound[7].

1-Amino-3-(p-fluoro)benzoylhydrazono-5-substituted-2-indolinones (III) : I (0.005 mole) was suspended in 10 ml of ethanol. To this suspension 1 ml of 37% formalin and amine (0.005 mole) were added with vigorous stirring. The mixture was heated on a water bath for 10 min and thereafter allowed to stand at room temperature overnight. The product thus deposited was filtered, washed well with ethanol and petroleum ether (60-80°) and dried well in air. It was finally recrystallised from chloroform or carbon tetrachloride and petroleum ether (60-80°) or ethyl acetate (Table 3).

3-Arylimino-2-indolinones (IV) : Isatin (0 01 mole) was taken in 25 ml of absolute ethanol containing 2-3 drops of glacial acetic acid and aryl amine (0.01 mole) was added to it. The reaction mixture was refluxed for 5 hr. The product was recrystallised from ethyl acetate.

Pharmacology :

CNS activity : Thirteen compounds out of the 16 synthesised were examined for their toxicity tests and the gross CNS activity at 1/5th of ALD_{50}, by the method of Wiel[15] (Table 4).

The compounds have been found to be non-toxic and psychotropic agents. Compound No. 4

TABLE 4—CNS ACTIVITY

Compound No.	ALD_{50}	SMA	Gross effect at 1/5th of ALD_{50}		
			SA Reactivity	Writhing	Body temp.
2	825	—	—	(+)	—
4	681	↓	↓	(+)	0.2°
5	1000	↓	↓	(+)	—
6	1000	—	—	(+)	—
7	681	—	—	(+)	0.2°
8	1000	↑	↑	(−)	(−)
9	1000	↑	↑	(−)	(−)
10	1000	↑	↑	(−)	(−)
11	1000	↑	↑	(−)	(−)
13	1000	↑	↑	(−)	(−)
14	1000	↑	↑	(−)	0.6°
15	681	↑	↑	(−)	0.2°
16	1000	↑	↑	(−)	0.4°

and 5 have been found to be CNS depressant whereas the remaining tested compounds have shown an increase in SMA and reactivity to sound and touch. Compound No. 2 and 4 to 7 have induced writhing, showing some muscle relaxant effect on belly muscles. Compound No. 4, 7 and 14 to 16 have induced hypothermia ranging between 0.2 to 0.6°. Rest of the compounds were ineffective towards body temperature.

Antibacterial activity : The method of Varma and Nobles[16] was employed for determining the antibacterial spectrum of all the compounds. The test organisms included *Bacillus megaterium, Xanthomonas malvacearium, Escherichia coli* and *Bacillus subtilis*. Sterile filter paper discs (5 mm diam), saturated with solution of the test compounds were placed on the agar [1.5% (w/v) agar ; 0.5% (w/v) NaCl ; 0.5 (w/v) glucose and 2.5% (w/v) peptone, pH 6.8-7.0] plates after drying up the solvent. The plates were incubated at 37° for 24 hr and zones of inhibition around the discs were measured. Bacterial cultures maintained at Public Analyst Laboratory, U. P. Government, Lucknow, were used (Table 5).

TABLE 5—ANTIBACTERIAL ACTIVITY

Sl. No.	*B. meg.*	*X. m.*	*E. coli*	*B. subtilis*
1.	+	+	+	+
2.	+	++	+	++
3.	++	+++	+	++
4.	+	++	+	+
5.	−	+	+	+
6.	−	+	++	+
7.	+	+	+	+
8.	−	+	+	++
9.	++++	++	+	+
10.	++++	+++	+	+
11.	++	+++	++	+
12.	++	−	−	−
13.	++++	++	+	+
14.	++++	+	−	+
15.	+++	+	−	+
16.	++	·	+	−

− = No inhibition , + = Zone size 6-8 mm , ++ = Zone size 8-10 mm , +++ = Zone size 10-15 mm , ++++ = Zone size > 15 mm.

Compound No. 9, 10, 13 and 14 were found to be most active against *B. megaterium* and *X. malvacearium*.

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Extraction and Spectrophotometric Determination of Vanadium(V) as Mixed Ligand Complexes of Various Hydroxyamidines and Thiocyanate**

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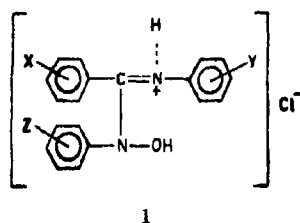
A simple and selective method for the extractive spectrophotometric determination of vanadium(V) in various alloy steels at micro-gram level has been developed The method is based on the chloroform extraction of vanadium(V) with eleven newly synthesized hydroxyamidines (HOA) and thiocyanate. The molar absorbances of the complexes lie between $3.30-6.25\times10^{3}$ l. mol^{-1} cm^{-1} at 595-610 nm with Sandell's sensitivities in the range 0 008-0.015 μg of metal per cm^{2}. In present investigation N-hydroxy-N-*p*-chlorophenyl-N'-(2,3-dimethyl)phenylbenzamidine hydrochloride was selected for a detailed study. It forms a deep green complex in the *p*H range 1.7-3.0 having the ratio 1 : 2 : 2 (V : SCN^{-} : HOA). Fe(III), Cu(II), Ni(II), Co(II) Zn(II), Cd(II), Mn(II), Cr(III), Ti(IV), Zr(IV), Nb(V), Mo(VI) W(VI), flouride, iodide, thiosulphate, oxalate, phosphate etc. do not interfere.

N-Hydroxy-N,N'-diarylbenzamidine (HOA) and its derivatives have been recently explored as potential reagents for the determination of various d-group elements[1-5]. HOA is a better reagent than other well known organic reagents[6-8], because of its high molecular weight and selective colour reaction towards the metal ions. However, there is considerable scope for improvement in the structural features of such a molecule to make it more suitable as an analytical reagent, as substitution is possible in three phenyl rings The objective of the present communication is to study the colour reaction of even newly synthesized N-hydroxy-N,N'-diarylbenzamidines (I), with vanadium(V) in presence of thiocyanate with a view to study the effect of substituents on the complexing properties of the $-N=C-N(OH)-$ group.

1

X = H –
Y = H –, *o*-CH_3 –, *m*-CH_3 –, *p*-CH_3 –, 2,3-$(CH_3)_2$ –, 2,5-$(CH_3)_2$ –, 2,6-$(CH_3)_2$ – or *p*-OCH_3 –
Z = H –, *m*-Cl –, *p*-Cl – or *p*-CH_3 –

N-Hydroxy-N-*p*-chlorophenyl-N'-(2,3-dimethyl)-phenylbenzamidine hydrochloride was found to be the most sensitive reagent in the present investigation and hence selected for the detailed study.

The advantages of the proposed method over the recommended methods[9-13] are that the colour reaction is simple, rapid, sensitive and fairly selective. The ions Mn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, Mo^{6+} and oxidizing agents do not interfere and there is no possibility of reduction of vanadium(V).

Experimental

Absorptiometric and *p*H-metric measurements were made with an ECIL, UV-VIS spectrophotometer, model GS-865 with matched 1 cm quartz and silica cells and Systronic *p*H-meter, type-322, respectively.

Vanadium(V) solution was prepared from ammonium metavanadate (B.D.H., AnalaR) and standardized volumetrically using potassium permanganate[14]. The reagent was prepared by the condensation of equimolar quantities of N-arylbenzimidoylchloride and N-arylhydroxylamine in ether medium[1].

A 0.1% (w/v) solution of hydroxyamidine in chloroform and 5% (w/v) solution of potassium thiocyanate in water were used for the extraction work.

Procedure : An aliquot of the vanadium(V) solution (100 μg V) and 2 ml of thiocyanate solution were taken in a 125 ml separatory funnel and the *p*H was maintained at 2.2 in final dilution of 15 ml using HCl-KCl buffer. The aqueous layer was equilibrated with 15 ml chloroform solution of the reagent for 1 min. The organic layer was transferred over anhydrous sodium sulphate in a

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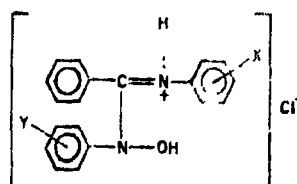
50 ml beaker. The aqueous phase was washed with 2×4 ml portions of chloroform. The combined extracts, after drying, were transferred to a 25 ml volumetric flask and the volume was made up to the mark with chloroform. The absorbances were measured at 605 nm against chloroform as a blank.

Results and Discussion

The absorption curve of reagent and its metal chelate showed that the reagent has negligible absorption in the region 450-700 nm, while the complex has a broad λ_{max} between 595-610 nm.

Effect of variables : Chloroform was chosen as a diluent for this study because of higher extractability of the complex and the reagent in it than other solvents (benzene, carbon tetrachloride and 2,4-dichlorobenzene). The *p*H of the aqueous phase was maintained with 1 *M* hydrochloric acid and dilute ammonia The optimum *p*H range for complete extraction of metal was found to be 1.7-3.0. At least 8 and 10 fold molar excess of hydroxyamidine and thiocyanate respectively were necessary for complete extraction of the metal. Addition of more reagent caused no adverse effect either in the position of λ_{max} or on the absorbance value of the complex. The order of addition of reagents was not critical. A time of 1 min was sufficient for complete extraction of vanadium(V). The complex was stable for atleast 40 hr at room temperature. Variation in temperature from 20 to 40° and volume of the aqueous phase from 15 to 60 ml had no effect on the nature of the complex. No effect of electrolytes (i.e. NaCl, KCl and NH_4Cl) upto 3 *M* on the distribution coefficient of the metal was observed.

Effect of substituents : The influence of substituents on the complexing properties of the ligand was studied by preparing eleven new analogues of N-hydroxy-N,N'-diarylbenzamidines and testing their potentialities in the extractive separation and spectrophotometric determination of vanadium(V). The molar absorptivities of the mixed ligand complexes were calculated on the basis of vanadium content at respective λ_{max} as shown in Table 1. It is observed that the position of λ_{max} is not appreciably effected by the substitution of N-phenyl or N'-phenyl ring. However, the absorptivity of the complex is affected markedly by the substitution of both phenyl rings. An alkyl group, introduced in the N'-phenyl ring, greatly affected the absorptivity of the complex. The substitution of this phenyl ring resulted into hyperchromic shift, the order being 2,5-$(CH_3)_2$>2,3-$(CH_3)_2$> *o*-CH_3> *p*-CH_3> *m*-CH_3 (Comp. 1-4, 6 and 8), and hypochromic shift in the order 2,6-$(CH_3)_2$>*p*-(OCH_3) (Comp. 1, 5 and 7). The substitution of N-phenyl ring also showed hyperchromic shift in the order *p*-Cl>*m*-Cl>*p*CH_3 (Comp. 8-11).

TABLE 1—SPECTRAL DATA OF VANADIUM (V)-THIOCYANATE COMPLEXES WITH HYDROXYAMIDINES IN CHLOROFORM

Sl. No.	X	Y	λ_{max} nm	ϵ l.mol^{-1}cm^{-1}	Sandell's sensitivity μg V cm^{-2}
1.	H –	*m*-Cl –	595	4800	0.01061
2.	*o*-CH_3 –	*m*-Cl –	600	5400	0.00948
3.	*m*-CH_3 –	*m*-Cl –	600	4800	0.01061
4	*p*-CH_3 –	*m*-Cl –	595	4800	0.01061
5	*p*-OCH_3 –	*m*-Cl –	595	4700	0.01088
6.	2,5-$(CH_3)_2$ –	*m*-Cl	600	6100	0.00835
7.	2,6-$(CH_3)_2$ –	*m*-Cl –	600	3800	0.01548
8.	2,3-$(CH_3)_2$ –	*m*-Cl	600	6000	0.00849
9	2,3-$(CH_3)_2$ –	H –	600	5250	0.00970
10.	2,3-$(CH_3)_2$ –	*p*-CH_3 –	610	5650	0.00901
11	2,3-$(CH_3)_2$ –	*p*-Cl –	605	6250	0.00815

No. 1, 4 and 5 are free bases.

As expected from the above observation, N-hydroxy - N - *p*-chlorophenyl-N'-(2,3-dimethyl)phenylbenzamidine hydrochloride is found to be the most sensitive reagent in the present investigation.

Concentration ranges, molar absorbance, sensitivity and precision of the method : The effective molar absorptivities of the coloured complexes lie in the range of 3.30 – 6.25 × 10^3 l. mol^{-1} cm^{-1} and the sensitivities[15] of the reaction lie between 0.008-0.015 μg V cm^{-2} as shown in Table 1. The method obeys Beer's law upto 7.2 ppm of vanadium. The optimum concentration range on the basis of Ringbom plot[16] lie between 1.2-6.8 ppm of the metal. The mean absorbance value and relative standard deviation of the method are found to be 0.490 and ± 0.67%, respectively (results of 10 measurements, each containing 100 μg V/25 ml).

Composition of the complex : The ratio of vanadium(V) to hydroxyamidine of thiocyanate was studied by mole ratio[17], slope ratio[18] and Job's method of continuous variation[19]. The results obtained indicated that the complex consists of 2 molecules each of hydroxyamidine and thiocyanate for each molecule of vanadium. The probable composition of the neutral mixed complex is VO.2SCN.OA.HOA.

Effect of diverse ions : The effect of various ions in the separation and subsequent spectrophotometric determination of vanadium(V) was studied, following the recommended procedure. Chloride, bromide, nitrate, sulphate, borate, phosphate, triethanolamine, alkali and alkaline-earth elements did not interfere upto 2000 ppm. Fe(III) interfered due to coextraction of its ternary complex but its interference could be eliminated by masking it with trisodium phosphate. Mo(VI) is also coextracted

as a binary yellowish complex but did not interfere at the absorption maxima. The interference of Cu(II) was eliminated by masking it with thiourea. The tolerated amount* of other ions (in ppm), in the determination of 4 ppm of vanadium(V) are shown in parenthesis: Cd^{2+}, Zn^{2+} (1000); Cu^{2+} (1200); Ni^{2+} (500); Co^{2+} (400); Mn^{2+} (600); Cr^{3+} and Al^{3} (500 ppm); Cs^{3+}, Rb^{+}, La^{3+} (1000); Fe^{3+}, Bi^{3+}, Th^{4+} (800); Zr^{4+} (80), Ti^{4+} (80); Nb^{5+} (60); Mo^{6+} (80); W^{6+} (40); U^{6+} (400); F^- (400); I^- (500); IO_3^- (100); arsentate (400).

Application of the method: The method has been applied successfully to three BCS steels, two V-W steels (64a and 241/1) and one tungsten free steel (252). The results of the determinations are summarized in Table 2.

TABLE 2— DETERMINATION OF VANADIUM IN VARIOUS BCS STEELS

Sample	Vanadium found[a] %	Certified %	Standard deviation
64a Alloy steel	1.553	1.57	± 0.0005
241/1 High speed steel	1.551	1.57	±0.0051
252 Low alloy steel	0.450	0.46	±0.0064

a = An average of six determinations
BCS = British Chemical Standards, Bureau of Analysed Samples Ltd, Newham Hall, Middlebrough, Yorks.

The sample containing about 2 mg of vanadium was dissolved in dilute nitric acid and oxides of nitrogen were removed by boiling. The insoluble matters were removed by filtration. The filtrate was made up to 250 ml in a volumetric flask and vanadium content of the sample was determined as mentioned in the recommended procedure.

* Error less than 2%.

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NOTES

A Study of the Decomposition Patterns of Some Transition Metal Complexes Derived mainly from the Heterocyclic Ligands viz., Furan-2-carboxaldoxime and 3-Methyl-4-arylazopyrazole-5-one using Thermogravimetric Analysis

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AMONG the methods finding extensive use in characterisation of transition metal complexes, TGA is one of the most recent methods. Besides indicating the presence of coordinating groups in a complex molecule, it describes in detail the decomposition pattern for the complex. In the present paper the TGA data in the temperature range 20-800° of some complexes of Cu(II), Ni(II) and Co(II) containing either of the two title ligands along with one or more water molecules and an heterocyclic amine or diamine, are described.

Experimental

The two types of complexes used in the study are derived from either the neutral or the anionic form of antifuran-2-carboxaldoxime or 3-methyl-4-(*p*-methylphenylazo)pyrazole-5-one as primary ligand and water, pyridine (py), picoline (pic), aniline (an), ethylenediamine (en), propylenediamine (pn), 2-2′-bipyridyl (bipy) or *o*-phenanthroline (phen) as secondary ligand. The preparation and characterisation of the complexes were reported in a previous communication[1-3]. The Cu(II) complexes were assigned planar and Ni(II) and Co(II) complexes octahedral structure, respectively.

Results and Discussion

Complexes derived from antifuran-2-carboxaldoxime : The various complexes which have been subjected to TGA study are of the type [Co or Ni(FDH)$_2$ dam]Cl$_2$; [Co(FDH)$_3$](NO$_3$)$_2$; [Ni(FD)$_2$dam] where FDH and FD refer to the neutral and the anionic form of the oxime and dam stands for ethylenediamine (en), propylenediamine (pn), 2-2′-bipyridyl (bipy) or *o*-phenanthroline (phen)[1-3]. The general decomposition pattern of some of the complexes of different categories is as given below.

It appears from the above equations that in most of the complexes a slight decomposition

(i) $$[Ni(FDH)_2en]Cl_2.2H_2O \xrightarrow[-2H_2O]{100\text{-}120^\circ} [Ni(FDH)_2en]Cl_2 \xrightarrow[\%\ loss = 15.37\ (15.81)]{-Cl_2} [Ni(FDH)_2en] \xrightarrow[-(FDH+en)]{280\text{-}400^\circ} NiO \text{ at } 500^\circ$$

% loss = 7.10 (8.03)

(ii) $$[Co(FDH)_2dam]Cl_2.2H_2O \xrightarrow[-2H_2O]{100\text{-}120^\circ} [Co(FDH)_2dam]Cl_2$$

% loss = 7.00 (7.70)

$$\xrightarrow[-Cl_2]{180\text{-}200^\circ} [Co(FDH)_2dam] \xrightarrow[-(FDH+dam)]{280\text{-}500^\circ} Co_3O_4 \text{ at } 520^\circ$$

% loss = 15.42 (15.31)

(iii) $$[Co(FDH)_3](NO_3)_2 \xrightarrow[-3FDH]{160\text{-}180^\circ} Co(NO_3)_2 \xrightarrow[-2NO_2]{280\text{-}450^\circ} Co_3O_4 \text{ at } 460^\circ$$

% loss = 64.25 (64.53) ; % loss = 24.10 (24.05)

(iv) $[Ni(FD)_2en].2H_2O \xrightarrow[-2H_2O]{100\text{-}120^\circ} [Ni(FD)_2en] \xrightarrow[-en]{220\text{-}240^\circ} Ni(FD)_2$

% loss = 8.96 (9.60); % loss = 15.32 (16.00)

$Ni(FD)_2 \xrightarrow{-FD}$ NiO at 380°; % loss = 28.23 (29.39)

begins at 80 or 100° and continues up to 120° and corresponds to the loss of water. This is the range in which the lattice water is lost and hence these water molecules are not coordinated as indicated in the formulae of complexes. No decomposition occurs between 120-180°. The two chloride ions are lost between 180-200°. From 220° to 280° there is a very sharp decrease in weight due to the loss of oxime and different amines. The complex is changed to the simple metal oxide above 500° and the curve then becomes a straight line.

Complexes derived from 3-methyl-4-(p-methylphenylazo)pyrazole-5-one : The TGA studies of the free azo compound (PyrH $C_{11}H_{12}N_4O$), its two complexes with Cu(II) and Ni(II) sulphates, free Cu(II) and Ni(II)-3-methyl-4-(*p*-methylphenylazo)-5-pyrazolonates $[M(C_{11}H_{11}N_4O)_2]$ and their complexes[4,5] with different amines are described in the following equations.

(i) Free $C_{11}H_{12}N_4O$ (PyrH) $\xrightarrow[\%\ loss=100]{400\text{-}440^\circ}$ decomposes completely.

(ii) $[Cu(PyrH)(H_2O)_2]SO_4 \xrightarrow[-2H_2O]{220\text{-}240^\circ} [Cu(PyrH)]SO_4 \xrightarrow[-PyrH]{380\text{-}420^\circ} CuSO_4$

% loss = 9.00 (9.40); % loss = 51.60 (52.00)

$CuSO_4 \xrightarrow[-SO_3]{500\text{-}600^\circ}$ CuO; % loss = 68.55 (69.55)

(iii) $[Ni(Pyr)_2].2H_2O \xrightarrow[-2H_2O]{100\text{-}120^\circ} [Ni(Pyr)_2] \xrightarrow[-PyrH]{180\text{-}240^\circ}$ NiO

% loss = 10.00 (11.50); % loss = 70 10 (71.70)

(iv) $[Ni(Pyr)_2an].2H_2O \xrightarrow[-2H_2O]{80\text{-}100^\circ} [Ni(Pyr)_2an] \xrightarrow[-an]{180\text{-}200^\circ} [Ni(Pyr)_2]$

% loss = 5.00 (5.74); % loss = 17.20 (18.13)

$[Ni(Pyr)_2] \xrightarrow[-Pyr]{340\text{-}400^\circ}$ NiO; % loss = 81.70 (80.00)

(v) $[Cu(Pyr)_2(pic)].H_2O \xrightarrow[-H_2O]{80\text{-}100^\circ} [Cu(Pyr)_2(pic)] \xrightarrow[-pic]{160\text{-}180^\circ} [Cu(Pyr)_2]$

% loss = 2.85 (3.29); % loss = 14.19 (13.00)

$[Cu(Pyr)_2] \xrightarrow[-Pyr]{340\text{-}380^\circ}$ CuO; % loss = 71.54 (70.00)

(vi) $[Ni(Pyr)_2(phen)] \xrightarrow[-phen]{160\text{-}180^\circ} [Ni(Pyr)_2] \xrightarrow[-pyr]{380\text{-}410^\circ}$ NiO

% loss = 24.80 (25.10); % loss = 64.50 (65.50)

It appears from the above equations that the lattice water is lost between 80-120°, while the co-ordinated water is lost at slightly higher temperature around 280°. The coordinated amine usually decomposes in the range 140-200°, the individual temperature, however, varies with the nature of amine and complex. The azo groups are lost completely around 380° and thereafter, the formation of the metal oxide occurs and no decomposition takes place upto 1000°.

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Mixed Ligand Complexes of Zinc(II) with Dibasic Acids and Nitrogen Donor Ligands

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AS a part of the programme on d^{10} metal complexes, some penta-coordinated zinc(II) complexes with nitrogen and sulphur donor ligands were reported[1-3] earlier from this laboratory. More recently Sharma and Jain reported[4] some mixed ligand complexes of nickel(II) with dibasic acids and primary and heterocyclic amines as secondary ligands. This communication reports some penta-coordinated mixed ligand complexes of zinc(II) succinate, malonate, glutarate or adipate with thiocyanate and nitrogen donor ligands like α-picoline and morpholine.

Experimental

Ethanolic solutions of zinc chloride, the organic acid and potassium thiocyanate were mixed in stoichiometric ratio and filtered directly into an ethanolic solution of α-picoline or morpholine. The resulting precipitate was suction filtered, washed with ethanol and ether, recrystallised from carbon tetrachloride/methanol and dried *in vacuo*.

Zinc, thiocyanate and nitrogen were estimated by standard methods. Carbon and hydrogen were microanalysed. The conductance measurements were carried out on 10^{-3} *M* solutions in pyridine using Toshniwal conductivity bridge, type CL 0102, with a dip type cell. Infrared spectra were recorded in the region 4000-400 cm^{-1} by Perkin Elmer spectrophotometer in KBr pellets. Thermogravimetric studies[3] were carried out in a manually operated thermobalance. Analytical and physical data for the complexes are recorded in Table 1.

As the α-picoline complexes take up moisture and decompose due to hydrolysis, these were kept in a desiccator over anhydrous $CaCl_2$.

Results and Discussion

The molar conductance values (Table 1) of al the compounds indicate them to be 1 : 1 electrolytes In the ir spectra, the stretching bands due to C=O of malonic, succinic, glutaric and adipic acids at 1724, 1730, 1695 and 1700 cm^{-1}, respectively have been lowered to 1630, 1635, 1630 and 1610 cm^{-1} in the corresponding complexes indicating the coordination of acids through carboxylate oxygen[4] The bands appearing at 2050-2080 and 785-860 cm^{-1} due to ν (C–N) and ν (C–S), respectively indicate the presence of N-bonded thiocyanate group[5] The bands at ~3210 and ~1115 cm^{-1}, due to

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF MIXED LIGAND ZINC(II) COMPLEXES

Compound	m.p. °C	%Zn	%thio-cyanate	%N	%C	%H	Λ_M mhos≠
K[Zn(α-pic)M.H_2O(NCS)]	210(d)	17.23 (17.41)*	15.2 (15.46)	7.55 (7.41)	31.81 (31.78)	3.01 (2.93)	66
K[Zn(α-pic)S.H_2O(NCS)]	200(d)	16.52 (16.79)	14.76 (14.89)	7.00 (7.17)	33.67 (33.88)	3.42 (3.36)	68
K[Zn(α-pic)G.H_2O(NCS)]	230(d)	16.02 (16.20)	14.27 (14.37)	6.78 (6.90)	35.34 (35 51)	3.90 (3 72)	74
K[Zn(α-pic)A.H_2O(NCS)]	250(d)	15.41 (15.65)	13 76 (13.90)	6.42 (6.67)	37.00 (37.18)	3.8 (4.0)	70
K[Zn(moph)M.H_2O(NCS)]	112	17.42 (17.69)	15.58 (15.73)	7 67 (7.57)	26.74 (26.98)	3.62 (3.54)	71
K[Zn(moph)S.H_2O[NCS)]	105	16.88 (17.05)	15.01 (15.12)	7.29 (7.30)	27.98 (28.16)	4 08 (3.94)	69
K[Zn(moph)G.H_2O(NCS)]	138	16.27 (16.45)	14.51 (14.60)	6.86 (7.04)	30.00 (30.19)	4 50 (4.31)	78
K[Zn(moph)A.H_2O(NCS)]	172	15.66 (15.89)	14.00 (14.10)	6.57 (6.80)	31.84 (32.06)	4.74 (4.65)	75

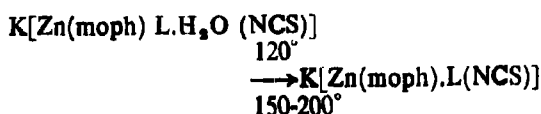
* Figures in parentheses indicate calculated values. M=malonate, S=succinate, G=glutarate and A=adipate, α-pic=α-picoline, moph=morpholine, d=decomposed.

≠ Based on theoretical values of molecular weight.

ν(N – H) stretch and ν (C – O – C) stretch show – ve and +ve shift respectively with respect to free morpholine and indicate morpholine coordinates through nitrogen atom[6]. Similarly, the sharp bands at ~2940 and ~1040 cm^{-1} are attributed to the presence of N-coordinated α-pic[7]. The broad band at ~3400 cm^{-1} and sharp band at ~870 cm^{-1} in both the complexes indicates the presence of coordinated water molecule[5].

Thermal decomposition : Thermal decomposition of morpholine complexes reveals no weight loss at 100° indicating that the water molecules are not in the lattice. The different products from the weight loss obtained by thermal decomposition are as follows :

$$K[Zn(moph)\,L.H_2O\,(NCS)] \xrightarrow{120^\circ} K[Zn(moph).L(NCS)]$$

$$K[Zn(moph).L(NCS)] \xrightarrow{150\text{-}200^\circ} KSCN + ZnL$$

where L = anion of dibasic acids.

In the light of the above evidences, it is suggested that all the complexes are five coordinated anionic complexes.

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Mixed Ligand Complexes of Cobalt(II) and Cadmium(II) with Oxine as Primary Ligand and Heterocyclic and Aromatic Amines as Secondary Ligands

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OXINE is known to possess both antifungal and antibacterial properties[1-3]. It also behaves as an uninegative bidentate chelating ligand having ON potential donor sites. The present note describes the synthesis and characterisation of some mixed ligand complexes of cobalt(II) and cadmium(II) with nitrogen donor heterocyclic and aromatic bases.

Experimental

All the chemicals used were of A.R. grade.

Preparation of metal oxinates : To an aqueous solution of metal chloride (2.36 g in case of cobaltous chloride and 2.01 g in case of cadmium chloride), sodium acetate (5 g) was added and warmed to 65-70°. The ethanolic solution of oxine (3.0 g) was added to it separately when light brown amorphous cobalt oxinate or light yellow amorphous cadmium oxinate separated out immediately. The metal oxinates thus formed were allowed to stand overnight and then filtered, washed with ethanol followed by ether and dried *in vacuo*.

Preparation of mixed ligand complexes : To an ethanolic suspension of metal oxinate nitrogen donor ligands were added separately and refluxed for 1-2 hr. The compounds were then filtered, washed with ethanol, ether and dried *in vacuo*.

The metal contents of the complexes were estimated by EDTA titration method and nitrogen by microanalytical method. Conductance of the complexes was measured in 10^{-3} *M* acetone solution using a Toshniwal conductivity bridge. IR spectra were recorded on KBr phase using Beckman IR-20 spectrophotometer. Electronic spectra of cobalt(II) complexes were recorded in 10^{-3} *M* DMF-base solution using Hilgerwatt Uvispeck spectrophotometer. Analytical data of the complexes prepared are given in Table 1.

Results and Discussion

Complexes reported in the present investigation are of the type $[ML_2L'_2]$ and $[ML_2L'']$ where M = cobalt(II), cadmium(II) ; LH = oxine ; L' = pyridine, β-picoline, γ-picoline, quinoline, piperidine, 2,6-lutidine, 4-aminopyridine, quinaldine, morpholine ; L'' = *o*-phenylenediamine, 1,10-phenanthroline or 2-2'-bipyridine. The complexes show low conductance values in acetone medium (Λ_M ranges from 8.5 to 15 mhos cm^2) indicating their non-electrolytic nature.

IR spectra of the ligand, metal oxinate and mixed ligand complexes are informative. The ir active bands at 1500, 1280 and 900 cm^{-1} can be assigned to the phenolic OH deformation modes coupled with C – O stretching modes ($\nu_{CO}+\nu_{OH}$) and to the out of plane deformation vibration (σOH), respectively. The absence of these bands in the spectra of the metal oxinates indicates that the proton of the hydroxyl group is replaced by the metal ions. The bands at 1450, 1260, 1095 and 1060 cm^{-1} in the spectra of both heterocyclic ligands and mixed ligand complexes are characteristic of substituted pyridine ring vibration[4]. A medium broad band appears at ~3450 cm^{-1} region in case of metal oxinates assignable[5] to ν(O – H) or

TABLE 1—ANALYSIS AND MAGNETIC SUSCEPTIBILITY DATA

Sl. No.	Compound	% Metal Found (Calcd.)	% N Found (Calcd.)	μ_{eff} B.M.
1.	$CoL_2(Py)_2$	11.59 (11.66)	10.97 (11.09)	4.9
2.	$CoL_2(\beta\text{-Pic})_2$	11.00 (11.09)	10.48 (10.54)	5.1
3.	$CoL_2(\gamma\text{-Pic})_2$	10.97 (11.09)	10.52 (10.54)	4.9
4.	$CoL_2(Q)_2$	9.68 (9.73)	9.20 (9.25)	4.9
5.	$CoL_2(Pip)_2$	11.35 (11.39)	10.73 (10.83)	4.9
6.	$CoL_2(2,6\text{-Lut})_2$	10.48 (10.57)	10.02 (10.06)	5.0
7.	$CoL_2(Quin)_2$	9.27 (9.30)	8.76 (8.84)	4.8
8.	$CoL_2(4\text{-AP})_2$	10.94 (11.01)	10.38 (10.48)	4.9
9.	$CoL_2(Mor)_2$	11.26 (11.30)	10.63 (10.75)	4.9
10.	$CoL_2.o\text{-PhDA}$	12.88 (12.94)	12.27 (12.31)	4.9
11.	$CoL_2$1,10-Phe	11.08 (11.17)	10.58 (10.62)	5.0
12.	$CoL_2$2-2′-bipy	11.68 (11.71)	11.10 (11.13)	5.0
13.	$CdL_2(Py)_2$	19.95 (20.12)	9.97 (10.02)	—
14.	$CdL_2(\beta\text{-Pic})_2$	19.17 (19.23)	9.51 (9.58)	—
15.	$CdL_2(\gamma\text{-Pic})_2$	19.15 (19.23)	9.48 (9.58)	—
16.	$CdL_2(Q)_2$	16.94 (17.07)	8.43 (8.50)	—
17.	$CdL_2(2,6\text{-Lut})_2$	18.28 (18.41)	9.12 (9.17)	—
18.	$CdL_2(Pip)_2$	19.68 (19.70)	9.76 (9.81)	—
19.	CdL_2o-PhDA	22.04 (22.10)	10.97 (11.01)	—

Py = pyridine, β-Pic = β-picoline, γ-Pic = γ-picoline, Q = quinoline, Pip = piperidine, 2,6-Lut = 2,6-lutidine, Quin = quinaldine, 4-AP = 4-amino-pyridine, Mor = morpholine, o-PhDA = o-phenylenediamine, 1,10-Phe = 1,10-phenanthroline, 2-2′-bipy = 2-2′-bipyridine.

coordinated water molecules and its conspicuous absence in the mixed ligand complexes support the coordination of nitrogen donor ligands to the metal ions.

In the electronic spectra the cobalt(II) complexes in DMF solution give rise to two absorption bands with maxima around 8.6 and 19.7 kK region which can be assigned[6] to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F) and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transitions These absorption bands along with its magnetic moment values indicate a high-spin octahedral configuration for cobalt(II) complexes.

All the cadmium(II) complexes are six-coordinated on the basis of analysis, conductance and ir spectral studies.

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Complexes of Co(II), Ni(II), Cr(III), Mn(III) and Fe(III) with Schiff Bases Derived from *Bis-p*(Aminophenyl) Sulphide and 2-Acetyl Thiophene Glyoxal

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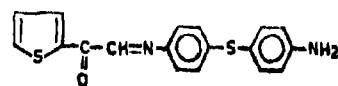
IN continuation to our work[1-3] on Schiff base complexes, present note describes the preparation and characterisation of complexes of Co(II), Ni(II), Cr(III), Mn(III) and Fe(III) with the Schiff base (I). Conductance, magnetic moment, electronic and infrared spectra of the complexes have been studied.

I

Experimental

The ligand was prepared by taking the *bis-p*(aminophenyl) sulphide and 2-acetyl thiophene glyoxal in dioxane in equimolar quantities and refluxing for about 1 hr. The refluxed mass was poured into ice cold water when an orange coloured mass separated out. It was dried in a vacuum desiccator and recrystallised from ethanol. Bright orange coloured fine crystals, m.p. 186°, were obtained.

A general procedure was adopted to synthesise the complexes by mixing Co(II), Ni(II), Cr(III), Mn(III) and Fe(III) chloride (10 m mole each) in 25 ml acetone with 10 m mole of the ligand separately. The reaction mixture was refluxed for 30 min and concentrated in a vacuum desiccator, yielding the coloured crystalline material. The crystals were washed with ether and dried.

The analysis of carbon, nitrogen and sulphur were done at the micro analytical section of C. D. R. I., Lucknow. The chloride was estimated by Volhard's method. The metal contents in all

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TABLE 1—ANALYTICAL DATA, FORMULAE AND OTHER PROPERTIES OF THE COMPLEXES

Complex	Colour	m.p. °C	Analysis % M	C	N	S	Cl	μ_{eff} B.M.
$[CoLCl_2.H_2O]$	grey	192d	12.47 (12.12)*	43.90 (44.45)	5.38 (5.76)	13.38 (13.17)	14.90 (14.61)	4.89
$[NiLCl_2.H_2O]$	dark green	167d	12.32 (12.08)	45.60 (44.47)	5.60 (5.76)	13.42 (13.17)	14.87 (14.60)	2.98
$[CrL_2]Cl_3$	black	189d	6.52 (6.23)	50.20 (51.76)	6.92 (6.71)	15.58 (15.33)	13.00 (12.76)	3.86
$[MnL_2]Cl_3$	grey	200d	6.60 (6.56)	51.42 (51.58)	6.70 (6.68)	14.20 (14.09)	12.76 (12.71)	4.80
$[FeL_2]Cl_3$	dark	208d	6.90 (6.66)	50.30 (51.53)	6.43 (6.67)	15.41 (15.26)	12.56 (12.30)	5.84

* Figures within the parentheses are Calcd. values L$-C_{18}H_{14}N_4S_2O$, d$-$decomposed.

TABLE 2—ELECTRONIC SPECTRA AND LIGAND FIELD PARAMETERS

Complex	Bands cm^{-1}	Assignments	10Dq cm^{-1}	B cm^{-1}	β	L.F.S.E. Kcals/mole
$[CoLCl_2.H_2O]$	9700	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	—	843	0.76	13.86
	17680	$\rightarrow {}^4A_{2g}(F)$				
	22000	$\rightarrow {}^4T_{1g}(P)$				
$[NiLCl_2.H_2O]$	10000	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	10000	886	0.82	34.28
	17756	$\rightarrow {}^3T_{1g}(F)$				
	26030	$\rightarrow {}^3T_{1g}(P)$				
$[CrL_2]Cl_3$	14250	$^4A_{2g}(F) \rightarrow {}^2E_g$	18400	700	0.82	31.54
	18400	$\rightarrow {}^4T_{2g}(F)$				
	23270	$\rightarrow {}^4T_{1g}(F)$				
	38400	$\rightarrow {}^4T_{1g}(P)$				
$[MnL_2]Cl_3$	17980	$^5B_{1g} \rightarrow {}^5T_{2g}$	17980	832	0.73	30.82
	13200	$\rightarrow {}^5A_{1g}$				
	11000	$\rightarrow {}^5B_{2g}$				
	29580	$\rightarrow {}^5E_g$				
$[FeL_2]Cl_3$	11780	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$	11780	786	0.56	—
	19380	$\rightarrow {}^4T_{2g}(G)$				
	27010	$\rightarrow {}^4T_{1g}(P)$				

TABLE 3—IR SPECTRA (cm^{-1})

L	$[CoLCl_2.H_2O]$	$[NiLCl_2.H_2O]$	$[CrL_2]Cl_3$	$[MnL_2]Cl_3$	$[FeL_2]Cl_3$	Tentative assignments
1260(w)	1245(w)	1246(w)	1220(w)	1220(w)	1230(w)	ν(C=S)
1650(s)	1630(s)	1635(s)	1590(s)	1610(s)	1610(s)	ν(CH=N)
1700(s)	1675(s)	1680(s)	1660(s)	1660(s)	1655(s)	ν(C=O)
—	485(m)	490(m)	460(m)	545(m)	540(m)	ν(M−O)
—	470(m)	475(m)	480(m)	470(m)	460(m)	ν(M−N)
—	350(s)	355(s)	375(s)	330(s)	325(s)	ν(M−S)
—	290(m)	275(m)	—	—	—	ν(M−Cl)

s = strong, m = medium and w = weak.

these complexes were estimated by complexometric titrations with EDTA[4]. The physical measurements viz., magnetic susceptibility (Gouy's balance), infrared spectra (Perkin-Elmer infrared spectrophotometer model-521, fitted with NaCl and KBr optics), absorption spectra (UNICAM SP-500 spectrophotometer) and molar conductance (Phillips conductivity bridge, type LBRB) were recorded at room temperature.

Results and Discussion

The complexes under investigation are listed in Table 1 along with their colour, analysis and other properties. The decomposition temperatures indicate that the complexes are thermally stable. The values of observed magnetic moments show the paramagnetic nature of the chelate and are in agreement with the generally accepted values for high spin octahedral complexes, thus forming sp^3d^2 type of bonding. The molar conductance of these complexes in DMF at 10^{-3} *M* indicates the non-electrolytic nature of Co(II) and Ni(II) complexes and unitrivalent nature of Cr(III), Mn(III) and Fe(III) complexes.

The electronic spectra (Table 2) of Co(II), Ni(II) and Fe(III) complexes show three bands appearing at 9700 cm^{-1} [$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$], 17580 cm^{-1} [$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$], 22000 cm^{-1} [$^4T_{1g}(F) \rightarrow$

$^4T_{1g}$ (P)], 10000 cm^{-1} [$^3A_{2g}$ (F)→$^3T_{2g}$ (F)], 17756 cm^{-1} [$^3A_{2g}$ (F)→$^3T_{1g}$ (F)], 26030 cm^{-1} [$^3A_{2g}$ (F)→$^3T_{1g}$ (P)] and 11780 cm^{-1} [$^6A_{1g}$→$^4T_{1g}$ (G)], 19380 cm^{-1} [$^6A_{1g}$→$^4T_{2g}$ (G)], 27010 cm^{-1} [$^6A_{1g}$→$^4T_{1g}$ (P)], respectively. The complexes of Cr(III) and Mn(III) show four bands in their electronic spectra appearing at 14250 cm^{-1} [$^4A_{2g}$ (F)→^2E_g], 18400 cm^{-1} [$^4A_{2g}$ (F)→$^4T_{2g}$ (F)], 23270 cm^{-1} [$^4A_{2g}$ (F)→$^4T_{1g}$ (F)], 38400 cm^{-1} [$^4A_{2g}$ (F)→$^4T_{1g}$ (P)] and 11000 cm^{-1} [$^5B_{1g}$→$^5B_{2g}$], 13200 cm^{-1} [$^5B_{1g}$→$^5A_{1g}$], 17980 cm^{-1} [$^5B_{1g}$→$^5\Gamma_{2g}$], 29580 cm^{-1} [$^5B_{1g}$→^5E_g], respectively. The values of β of these complexes indicate the partial covalent character of the metal-ligand bond.

Infrared spectral data for the ligand and its complexes are given in Table 3. ν(C−S), ν(CH=N) and ν(C=O) are lowered on complex formation by 15 to 45 units indicating that these groups are participating in chelation. Bands appearing at 230 cm^{-1} and 275 cm^{-1} in Co(II) and Ni(II) complexes, respectively are assignable to metal-chlorine stretching mode[5].

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Azo Complexes : Complexes of Alkali Metal Salts of Some Organic Acids with *o*-Hydroxybenzeneazo-2-Naphthol

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A series of mixed ligand adducts of alkali metal salts of different organic acids with *o*-hydroxybenzeneazo-2-naphthol, of the general formula MĿ.OHBAN (M=Li, Na or K; L=deprotonated organic acids; 1-nitroso-2-naphthol, 8-hydroxyquinoline, *o*-nitrophenol, 2-hydroxy-3-naphthoic acid, salicylic acid, salicylaldehyde; OHBAN=*o*-hydroxybenzeneazo-2-naphthol), have been synthesised. The adducts have been judged by their analytical results and infrared spectra, and this throws light on the fact that one molecule of alkali metal salt of organic acid combines with one molecule of ligand OHBAN, suggesting coordination number five or six for the metal atom.

Experimental

The ligand OHBAN was prepared by standard method[1], m.p. 194°. All the alkali metal salts used were prepared in 95% ethanol.

The general method of preparation was to take the hot absolute alcoholic solution of OHBAN and to add to it the alkali metal salts of organic acids in mono-molecular ratio. The whole mixture in solution was refluxed over water bath with stirring for about 1 hr. The solution, on keeping, yielded crystalline solid adducts. The crystals were filtered, washed with absolute alcohol and dried in an oven at 80°.

Results and Discussion

The adducts are stable when stored under dry condition e.g. in a desiccator. All the complexes are coloured (green, dark violet or brown). The compounds are thermally stable. When heated, they undergo a decomposition at a temperature higher than the melting point of the ligand. The adducts break on heating to form the simple salts and ligand, and this indicates that the bonding in these compounds is not strong. The colour, melting or decomposition temperatures and analysis of the complexes are given in Table 1.

The presence of two −OH groups in the *o, o'* positions to the azo group may increase the coordinating capacity of −N=N− group. It also suggests the possibility of intra-molecular hydrogen bonding due to which the metal is complexed in cyclic form.

TABLE 1

Compound	Colour	Melting / Decomp. temp °C	Found (%)				Calcd. (%)			
			C	H	N	M	C	H	N	M
OHBAN=L	Deep violet	194 m	72.69	4.55	10.61	—	72.72	4.54	10.60	—
Na1N2N.L	Dark violet	220 d	68.14	3.89	8.95	5.16	68.00	3.92	9.15	5.01
K1N2N.L	Dark violet	210 d	65.51	3.69	8.39	8.85	65.78	3.79	8.84	8.21
Na8HQ.L	Deep brown	280 d	70.48	4.10	9.51	5.09	70.40	4.06	9.48	5.19
K8HQ.L	Deep brown	215 d	67.92	3.94	9.48	8.14	68.00	3.92	9.35	8.50
NaONP.L	Green	223 d	62.09	3.81	9.95	5.40	62.12	3.76	9.88	5.41
KONP.L	Green	212 d	60.15	3 59	9.63	8.21	60.00	3.62	9.52	8.84
Na2H3NA.L	Brownish green	295 d	68.42	4.15	6.24	4.69	68.35	4.22	5.90	4.85
K2H3NA.L	Brownish green	290 d	66.42	3.91	6.11	7.59	66.12	3.88	5.71	8.00
Kacac.L	Green	208 d	62.92	4.45	5.82	9.95	62.68	4.72	6.96	9.70
Na.anth.L	Deep red	220 d	65.41	4.04	9.99	5.04	65.24	4.25	9.90	5.43
K.anth.L	Green	210 d	62 56	4.22	9.79	8.22	62.87	4.10	9.57	8.86
NaSalH.L	Brown	255 d	67.82	4 09	6.91	5.31	67.64	4.16	6.86	5.62
KSalH.L	Brown	242 d	64 92	4.12	6.98	8.75	65.10	4.00	6.60	9.20

OHBAN=*o*-hydroxybenzeneazo-2-naphthol, 1N2N=1-nitroso-2-naphthol, 8HQ=8-hydroxyquinoline, ONP=*o*-nitrophenol, 2H3NA=2-hydroxy-3-naphthoic acid, acac=acetylacetone, anth=anthranilic acid, SalH=salicylaldehyde.

Cenni *et al*[2] have reported that azo frequencies were usually observed in the range of 1570-1595 cm^{-1}. Bands in the region 1472-1545 cm^{-1} have been attributed to a number of aryl azo compounds of Mo by King[3]. In the ligand OHBAN, we obtain the $-N=N-$ band at 1550 cm^{-1}. In the adducts, this band shifts down to 1540-1515 cm^{-1} suggesting that the $-N=N-$ group is probably associated to the metal. These bands also split in the adducts which may be due to a change in symmetry. The $-N=N=$ frequency of ligand and its compounds with alkali metal salts have been given in Table 2.

TABLE 2—SELECTED IR FREQUENCIES OF LIGAND AND ADDUCTS

Compound	$-N=N-$ frequency (cm^{-1})
OHBAN=L	1550
Na1N2N.L	1540, 1535
K1N2N.L	1540,1535
Na8HQ L	1540, 1535
K8HQ.L	1535, 1530
NaONP.L	1540
KONP.L	1540
Na2H3NA.L	1535
K2H3NA.L	1535, 1530
Na.anth.L	1525, 1510
K.anth.L	1545, 1535
NaSalH.L	1540, 1525

The OH stretching frequency of the ligand has been observed at ~3360 cm^{-1}. It shifts down to ~3220 cm^{-1} in the compounds thereby showing the involvement of $-OH$ in the formation of adducts. The $H-O-H$ bending mode is seen at ~1300 cm^{-1} in the ligand, while in the compounds two peaks at ~1320-1310 cm^{-1} and at ~1280 cm^{-1} are observed. The extra peaks in complexes may justify their formation.

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Conductometric and Spectrometric Studies on Complexes of Ag(I) and Hg(II) Ions with N,N'-Diphenyl Thiourea

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SINCE N,N'-diphenylthiourea contains two phenyl substituent groups, the complexation behaviour of this ligand decreases[1-3] because of the electron withdrawing tendency of the phenyl group. In view of this, complexing behaviour of this ligand with Ag(I) and Hg(II) ions have been investigated in solution by conductometric titration and in solid state by infrared spectroscopy and the results are reported here.

Experimental

All chemicals used were of AnalaR quality. N,N'-Diphenylthiourea was prepared by standard method[4]. The prepared compound gave satisfactory C, H and N analysis.

Preparation of complexes: The diaquo N,N'-diphenylthiourea silver(I) nitrate polymeric complex, $\{[Ag(H_2O)_2(DPhTU)]NO_3\}_n$, was prepared by simply mixing an aqueous solution of $AgNO_3$ with ethanolic solution of N,N'-diphenylthiourea in 1 : 2 molar ratio. A green coloured precipitate formed immediately which was digested on water bath for 30 min. The complex was thereafter filtered, washed with ethanol and ether and dried at 110°. (Found : C, 35.90 ; H, 3.45 ; N, 9.41 ; Ag, 24.84. Calcd. C, 35.94 ; H, 3.69 ; N, 9.69 ; Ag, 24.90%).

The green aquochloro N,N'-diphenylthiourea mercury(II) chloride complex, $\{[Hg(H_2O)(DPhTU)Cl]Cl\}_n$, was prepared in the same manner as the Ag(I) complex. (Found : N, 5.84 ; Cl 13.43 ; Hg, 39 2%. Calcd. N, 5.41 ; Cl, 13.72 ; Hg, 38.8%).

Physical methods: The magnetic measurements were made at 30° using Guoy Balance. Both the complexes were found to be diamagnetic. The infrared spectra were recorded in KBr pellets using Perkin Elmer spectrophotometers, Model 521 and 621 in the range 4000-200 cm^{-1}. Conductometric titrations were carried out by means of Toshniwal conductometric bridge, model 302 using a dip type cell (cell constant 1.92×10^{-6} mho/cm^{2}).

Results and Discussion

The analytical results indicate that empirical formula of the solid complexes are $Ag(H_2O)(DPhTU)NO_3$ and $Hg(H_2O)(DPhTU)Cl_2$. The conductometric titrations of 0.01 *M* $AgNO_3$ and 0.01*M* $HgCl_2$ solutions were conducted against 0.005*M* diphenyl urea solution and inflexion points for both titrations indicate the formation of 1 : 1 complexes.

The Ag(I) complex contains ionic nitrate. This has been confirmed by chemical method as well as by the infrared spectra of the complex. The infrared spectra of this complex exhibit a strong band at 1385 cm^{-1} and a weak band at 845 cm^{-1}. These bands are not present in the spectra of the diphenylthiourea ligand or of the Hg(II) complex. Since ionic nitrates exhibit[5] strong infrared bands in the range of 1340-1410 cm^{-1} and weak band in the range of 800-860 cm^{-1}, it may be suggested that nitrate group is in the ionic form in the Ag(I) complex. But as the complex is insoluble in almost all organic solvents, it may be tentatively assigned a polymeric

formula, $\{[Ag(H_2O)_2(DPhTU)]NO_3\}_n$. Out of the two chlorine atoms in $Hg(H_2O)(DPhTU)Cl_2$, one is ionic. This is confirmed by the presence of Cl^- ion in the Na_2CO_3 extract of the complex. The other Cl atom is covalently bonded. This is also confirmed by the presence of ν(Hg – Cl) (terminal) band at 325 cm^{-1} in the infrared spectra of this complex. ν(Hg – Cl) (terminal) bands are generally observed[6-8] below this region in octahedral complexes. Thus, it may be concluded that Hg(II) ion is in tetrahedral coordination in this complex. But as the complex is insoluble in most organic solvents, the polymeric formulation, $\{[Hg(H_2O)(DPhTU)Cl]Cl\}_n$, may be suggested for it. The presence of coordinated water is confirmed[9-16] by the presence of bands at 3440, 1640, 530, 515 and 505 cm^{-1} in the Ag(I) complex and at 3500, 1645, 530, 515 and 505 cm^{-1} in the Hg(II) complex. Out of these five bands, the first two are assigned to νH_2O and δH_2O and the latter three to vibrational mode of coordinated water. More than one vibrational modes also confirm the polymeric nature of the complexes.

The diphenylthiourea ligand is bonded to the Ag(I) and Hg(II) ions in the two complexes through nitrogen as well as through thiocarbonyl sulphur. This is confirmed from the following considerations. (i) The splitting of ν(N - H) band of the ligand (3210 cm^{-1}) into two distinct bands at 3300 cm^{-1} and 3100 cm^{-1} indicating coordination through nitrogen. (ii) The bands of the ligand at 1595 and 1540 cm^{-1} observed as strong bands are assigned to $\delta NH + \nu CN$ modes. There is no change in intensity and position of these bands. This is possible only when there is no coordination or coordination occurs through both nitrogen and sulphur. (iii) The thioamide band II of the ligand is observed at 1340 cm^{-1} and is mainly due to ν(C = S) mode of vibration. This band has red shifted to 1320 cm^{-1} in the Ag(I) complex and 1315 cm^{-1} in the Hg(II) complex. This indicates coordination through sulphur. (iv) The thioamide band IV is observed at 760 cm^{-1} as a weak band[20] in the infrared spectra of the ligand. This band is found at the same position in the spectra of the complexes but its intensity increases on coordination. As coordination through sulphur red shifts this band[21-31] and coordination through nitrogen blue shifts it[21-31], it may be concluded that bonding has taken place both through sulphur and nitrogen. Increase in intensity may be due to polymeric nature of the complexes. (v) The far infrared spectra of the ligand contain only one weak band at 485 cm^{-1}. But the infrared spectra of the Ag(I) complex contain weak bands at 555 and 380 cm^{-1} which may be assigned to $\nu Ag \leftarrow OH_2$ and ν(Ag – N) modes of vibration. The infrared spectra of the Hg(II) complex contain new weak bands at 470, 325 and 300 cm^{-1}. These may be assigned to $\nu Hg \leftarrow OH_2$, ν(Hg – Cl) and ν(Hg N) modes of vibrations, respectively. As 325 cm^{-1} band is the strongest among the three bands, in has been assigned to ν(Hg – Cl). In monomeric tetrahedral complexes, ν(Hg – Cl) (terminal) is observed as a strong band in the 370 cm^{-1} region[26] but in linear 4-coordinated polymeric complexes, ν(Hg – Cl) (terminal) band is observed at 328 cm^{-1} as a strong and broad band[32]. As the metal – N and metal – S bonds are approximately of the same strength as indicated by equal red and blue shifts of thioamide band IV, ν (metal – S) mode is expected to be near 200 cm^{-1}. Hence, ν (metal – S) bands have not been observed.

Thus, the following tentative structures may be assigned to these complexes.
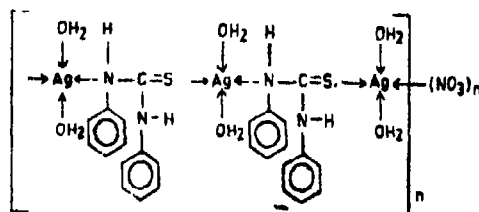
Fig. 1. Probable structure of $\{[Ag(H_2O)_2(DPhTU)]NO_3\}_n$.
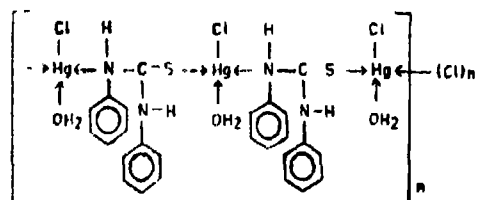
Fig. 2. Probable structure of $\{[Hg(H_2O)(DPhTU)Cl]Cl\}_n$.

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Determination of Stability Constants of 2-Hydroxy-1-naphthalidene-sulphafurazole Complexes with La^{3+}, Y^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+}, Dy^{3+}

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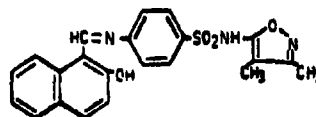
IN the present investigation, potentiometric studies on 2-hydroxy-1-naphthalidene-sulphafurazole and its complexes with some trivalent metal ions have been carried out. The dissociation constants (pK_1 and pK_2) of the reagent and the formation constants (log K_1 and log K_2) of its metal chelates have been determined potentiometrically following the Calvin-Bejerrum pH titration technique as adopted by Irving and Rossotti[1].

The titrations were carried out in 75 : 25 % (v/v) dioxane-water medium at 25±0.1° and at a constant ionic strength of 0.1 *M*. Appropriate correction factor for pH meter readings (B values) in 75% (v/v) dioxane-water medium has been applied[2].

Experimental

The ligand 2-hydroxy-1-naphthalidene-sulphafurazole was prepared by refluxing equimolar quantities of 2-hydroxy-1-naphthaldehyde and the amine in alcohol-DHF mixture for about 2 hr. The crude product was repeatedly crystallised from DMF to get an analytically pure compound with m p. 220°. The purity of the compound was established by tlc and elemental analysis. (Found : C, 63.21 ; H, 4.47 ; N, 10.24. Calcd. for $C_{22}H_{19}N_3O_4S$: C, 62.71 ; H, 4.51 ; N, 9.98%). The structure of the ligand is,

All the metal perchlorates used were prepared from metal carbonates and perchloric acid of A. R. grade. These were standardised complexometrically by EDTA titrations[3].

Other experimental details were the same as in earlier communication[4].

Results and Discussion

It may be mentioned here that the ligand did not undergo hydrolysis under the experimental conditions described. This was indicated by rapid attainment of equilibrium during the course of titration and by the absence of any significant drift in pH even after 2 hr. This was further confirmed by taking tlc of a sample titration mixture from time to time.

It is the phenolic (OH) group in the ligand which takes part in complex formation and the proton is replaced from it by the metal ion during chelation. As only one proton per ligand molecule is liberated, Y, the number of dissociable protons attached to each ligand molecule is one.

From the titration curves (Fig. 1), $\bar{n}_A$ values at various B values (pH meter readings) were calculated and the formation curve (B vs $\bar{n}_A$) was plotted. The pK_1 corresponding to phenolic H was obtained by half integral method of $\bar{n}_A=0.5$. This was further corroborated by plotting the graph of log ($\bar{n}_A/1-\bar{n}_A$) vs B.

From the titration curves (Fig. 1), $\bar{n}$ and pL values for metal-ligand systems were also determined. From the curves $\bar{n}$ vs pL, log K_1 and log K_2 values were determined by half integral method. As in the cases of La^{3+}, Gd^{3+} and Pr^{3+} complexes, the difference between log K_1 and log K_2 was found to be less than 1.78 log units. These were computed by least square method and the same are reported in Table 1.

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES

t=25° μ=0.1

Cations	H^+	Gd^{3+}	La^{3+}	Pr^{3+}	Nd^{3+}	Y^{3+}	Ly^{3+}
log K_1	7.763	8.19	7.90	7.55	5.60	5.30	5.06
log K_2	—	7.13	7.11	7.30	—	—	—

The order of stability of metal chelates is found to be $Gd^{3+}>La^{3+}>Pr^{3+}>Nd^{3+}>Y^{3+}>Dy^{3+}$.

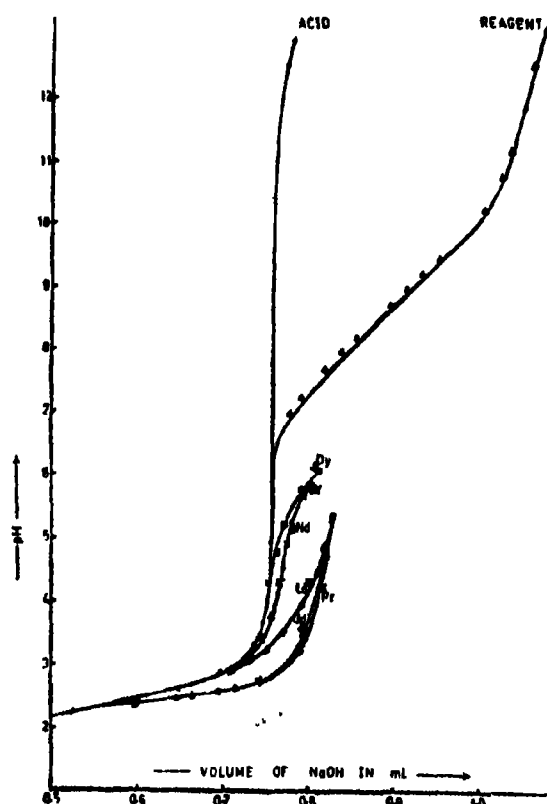



Fig. 1. Titration curves of 2-hydroxy-1-naphthalidene-sulphathiazole.

Acknowledgement

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Conductance of KCl and NaCl in Sucrose + Water, Glucose + Water and Urea + Water Mixtures at Different Temperatures

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STRUCTURAL interactions in ternary system comprising electrolyte-solvent-nonelectrolyte are gaining special attention in recent years. It has been observed that nonelectrolyte molecules interact with the ions of the electrolytes in solution[1-3]. Several polyhydroxy compounds are known to interact with electrolytes in solutions[1,4]. Definite adducts of many carbohydrates with salts and hydrated oxides of alkali and alkaline earth metals have also been reported[5,6]. Conductance of electrolyte solutions in the presence of nonelectrolytes have been measured by several workers[7-9]. The changes in conductance of carbohydrate-electrolyte solutions[10] was attributed to the obstruction of electrical migration of ions by the environmental nonelectrolyte entities[11,12].

In the present communication, the ion-solvent interaction of KCl and NaCl have been studied from conductivity data at weight percent of nonelectrolyte (sucrose, glucose) + water (5, 10, 15 and 20) mixtures at 30, 35, 40 and 45° and urea + water at 30 and 35°.

Materials and methods :

The salts used were of E. Merck 'Extra Pure' grade. Sucrose, glucose and urea were of B.D.H. AnalaR grade. The methods for preparation of the solvents and solutions and a measurements were the same as reported earlier[13]. Conductance measurement was of an accurary of ±2 in 1000. The concentration range was from 0.01 to 0.001 equiv/lit. Studies above 35° could not be performed in case of urea + water because of hydrolysis.

Results and Discussion

The equivalent conductivity of KCl and NaCl investigated at weight percent of nonelectrolyte (sucrose, glucose and urea) + water mixtures (5, 10, 15 and 20) are found to be linear with $C^{1/2}$ in the concentration range 0.01 to 0.001 mol lit^{-1}. This indicates that the salts are completely ionised. The limiting equivalent conductivity, Å, for KCl and NaCl at different compositions and at different temperatures obtained from the usual extrapolation procedure are given in Table 1 along with the values in aqueous solution[14].

From the determined Å values, the theoretical slope, S_T, of the plot of A vs $C^{1/2}$ at 35° for KCl and NaCl at different solvent compositions has been obtained and compared with the observed slope, S (Table 2). The S value is found to be greater than S_T, which indicates that the observed conductance is less than that of the theoretical value. This difference is of the order : sucrose + water > urea + water > glucose + water, which indicates the structure breaking order also.

The Walden product, $Å\eta_0$, has been usually employed to study ion-solvent interaction in solution from the conductivity data. $Å\eta_0$ of both KCl and NaCl at different temperatures and at different solvent composition are given in Table 3. The results show that it is maximum in case of glucose +

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TABLE—1

$\mathring{\Lambda}/\Omega^{-1}\ cm^2$

Temp. / Mass fraction of nonelectrolyte	Sucrose+water 30	Sucrose+water 35	Sucrose+water 40	Sucrose+water 45	Glucose+water 30	Glucose+water 35	Glucose+water 40	Glucose+water 45	Urea+water 30	Urea+water 35
KCl										
5	160.00	174.8	189.0	202.8	160.0	174.2	186.6	203.0	167.6	181.8
10	150.90	159.9	173.2	186.4	150 0	163.8	176.2	188.3	165.0	177.0
15	135.8	145.6	159.6	171.2	136.7	147.0	161.1	172.6	162.4	176.0
20	121.0	133.4	144.0	154.2 *149.86	123.5	134.9	145.6	156.7	151.8	163.0
NaCl										
5	139.5	153.8	169 0	181.6	141.4	153.4	169.0	183.8	149.0	161.8
10	129.4	142.8	154.0	167.6	131.5	144.4	156.2	169.2	145.0	158.8
15	114.2	135.6	136.8	140.6	110.4	127.6	138.8	149.6	137.8	150.6
20	103.2	118.8	123.9	134.6 *120.46	105.4	115.7	126.6	137.0	130.4	142.9

* Values at 25°[14]

TABLE 2—SLOPE VALUES (at 35° only)/$mol^{-1/2}cm^{7/2}$

	5% Sucrose S	5% Sucrose S_T	10% Sucrose S	10% Sucrose S_T	15% Sucrose S	15% Sucrose S_T	20% Sucrose S	20% Sucrose S_T
KCl	104.2	99.4	105.2	99.6	106.3	99.8	106.9	100.2
NaCl	100.9	95 2	101.4	96.2	103.3	97.4	103.4	98.3
	5% Glucose		10% Glucose		15% Glucose		20% Glucose	
KCl	102.7	99.4	103.6	99.5	104.6	99.9	105.6	100.8
NaCl	99.6	96.2	99.9	96.2	100.8	97.4	101.6	98.2
	5% Urea		10% Urea		15% Urea		20% Urea	
KCl	103.00	99 4	104.2	99.5	105 5	99.9	106.2	100.3
NaCl	100.40	96.0	100.8	96.0	101.2	97.3	102.6	97.8

TABLE 3—$\mathring{\Lambda}\eta_0/\Omega^{-1}\ cm^2\ P$

Temp. / Mass fraction of nonelectrolyte	Sucrose+water 30	Sucrose+water 35	Sucrose+water 40	Sucrose+water 45	Glucose+water 30	Glucose+water 35	Glucose+water 40	Glucose+water 45	Urea+water 30	Urea+water 35
KCl										
5	1.967	2 098	2.107	2.224	2.464	2.917	3.467	4.155	2.312	2.727
10	2 327	2 440	2.643	2.790	2.865	3.380	4.035	4.726	2.492	2.938
15	2.729	2.822	3.093	3.201	3.527	4 201	5.333	5.558	2.598	3.027
20	3.025	3.308	3.470	3.667	3.693	4.357	5.169	6.049	2.778	3.195
NaCl										
5	1.716	1,846	1 884	2.017	2.177	2.562	3.160	3.789	2.056	2.427
10	1 992	2 171	2.325	2.514	2 511	2.959	3.577	4.246	2.189	2.636
15	2 284	2 437	2.586	2.741	3.003	3.560	4.305	4.817	2.205	2.605
20	2.580	2.822	2.986	3.208	3.151	3.725	4.494	5.288	2.386	2.801

TABLE 4—DIFFERENCE IN $\mathring{\Lambda}/\Omega^{-1}\ cm^2$

Temp. / Mass fraction of nonelectrolyte	Sucrose+water 30	Sucrose+water 35	Sucrose+water 40	Sucrose+water 45	Glucose+water 30	Glucose+water 35	Glucose+water 40	Glucose+water 45	Urea+water 30	Urea+water 35
5	20.5	21.0	20.0	21.2	18.6	20.8	17.6	19.7	18.6	20.0
10	21.5	17.1	19.6	18.8	18.5	18.9	20.2	19.1	20.0	18.2
15	21.6	20.0	22.8	24.6	20.3	19.4	22.3	23.0	24.4	25.4
20	17.8	19.6	20.1	19.6	18.1	19.2	19.0	19.7	21.4	20.1

water and minimum in case of sucrose + water, urea + water being in between the two. Hence, the ion-solvent interaction is of the order :

sucrose + water > urea + water > glucose + water.

A better insight of the ion-solvent interaction can be obtained if the differences in the conductivity of KCl-NaCl at different compositions and at different temperatures be compared. These differences are recorded in Table 4. The differences are

not constant. The deviation from constancy in case of sucrose + water is maximum and least in case of glucose + water, whereas urea + water is in between the two. The more the deviation, the greater is the ion-solvent interaction[1,8]. So the order of ion-solvent interaction is sucrose + water > urea + water > glucose + water.

The above observations can be explained as follows. Sucrose contains more hydroxy groups than d-glucose and these hydroxy groups present in the compounds participate in the formation of hydrogen bonds with water molecules and hence the water structure breaks. Sucrose, therefore, is a stronger structure breaker than glucose. As regards urea, it can be said that urea is alkaline in water and acts both as a proton donor and acceptor, and hence in the mixture of urea and water, the structure in likely to be broken. Secondly, due to keto-enol tautomerism in solution urea may contain one hydroxy group which participates in the formation of hydrogen bond with water molecules and structure breaking is observed.

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Synthesis of Some 5-Arylazopyrimidine Derivatives

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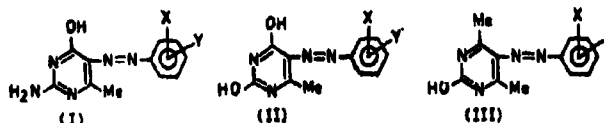
IN continuation of our work on the synthesis of 5-arylazopyrimidine derivatives of biological interest[1], we report here the synthesis of three more series of compounds, namely 2-amino-5-arylazo-4-hydroxy-6-methylpyrimidines (I), 5-arylazo-2,4-dihydroxy-6-methylpyrimidines (II) and 5-arylazo-4,6-dimethyl-2-hydroxypyrimidines (III).

All the compounds (I, II and III) were synthesised in excellent yields by the reaction of different aryldiazonium chlorides with appropriately substituted pyrimidine derivatives. The structures of the compounds were confirmed by their elemental analysis and ir spectra (bands in the region 1630-1590 cm^{-1} due to $-N=N-$ stretching). The arylazo group at position-5 was further confirmed by reducing three arylazo derivatives (one from each series) with Zn and AcOH. 2-Amino-4-hydroxy-6-methyl-5-phenylazopyrimidine (I, X = Y = H), on reduction, afforded 2,5-diamino-4-hydroxy-6-methylpyrimidine while II (X = Y = H) and III (X = Y = H) gave 5-amino-2,4-dihydroxy-6-methylpyrimidine and 5-amino-4,6-dimethyl-2-hydroxypyrimidine, respectively.

Experimental

Melting points were taken in open capillary in a sulphuric acid bath and are uncorrected. IR spectra were recorded on a Beckman IR-20 spectrophotometer as nujol mulls.

2-Amino-4-hydroxy-6-methylpyrimidine[2], 2,4-dihydroxy-6-methylpyrimidine[3] and 4,6-dimethyl-2-hydroxypyrimidine[4] were prepared by the methods described in literature and coupled with different aryl diazonium chlorides according to the method reported earlier[1]. All the compounds were crystallized from DMF-ethanol mixture. The characteristics of compounds belonging to series I, II and III have been listed in Tables 1, 2 and 3, respectively.

TABLE 1—CHARACTERISTICS OF 2-AMINO-5-ARYLAZO-4-HYDROXY-6-METHYLPYRIMIDINES (I)

Sl. No.	X,Y	m.p °C	Yield %	Analysis %		
					Calcd.	Found
1.	H	297d	75	N,	30.57	30.24
2.	2-CH_3	302	52	N,	28.80	28.64
3.	3-CH_3	316d	65	N,	28.80	28.68
4.	4-CH_3	299	48	N,	28.80	28.89
5.	2-OCH_3	307d	63	N,	27.03	27.13
6.	3-OCH_3	288	72	N,	27.03	27.00
7.	4-OCH_3	298d	70	N,	27.03	26.92
8.	4-OC_2H_5	206	50	N,	25.64	25.50
9.	2-Cl	128	78	Cl,	13.47	13.28
10.	4-Cl	288	80	Cl,	13.47	13.26
11.	2-Br	266	76	Br,	26.00	26.10
12.	4-Br	245	74	Br,	26.00	25.90
13.	2-NO_2	301	80	N,	30.56	30.49
14.	3-NO_2	314d	81	N,	30.56	30.49
15.	4-NO_2	319d	81	N,	30.56	30.46
16.	3,5-$(CH_3)_2$	315	61	N,	27.23	27.28
17.	2,4-$(Cl)_2$	299	65	Cl,	23.82	23.78

d = melts with decomposition.

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TABLE 2—CHARACTERISTICS OF 5-ARYLAZO-2,4-DIHYDROXY-6-METHYLPYRIMIDINES (II)

Sl. No.	X, Y	m.p. °C	Yield %	Analysis% Calcd.	Found
1.	H	302-4	73	N, 24.35	24.67
2.	2-CH_3	207-9	50	N, 22.95	22.85
3.	3-CH_3	179^d	54	N, 22.95	22.91
4.	4-CH_3	185^d	50	N, 22.95	23.07
5.	2-Cl	203-4	75	Cl, 13.42	13.49
6.	3-Cl	172	77	Cl, 13.42	13.28
7.	4-Cl	235^d	73	Cl, 13.42	13.44
8.	2-Br	205	78	Br, 25.89	26.10
9.	4-Br	220^d	75	Br, 25.89	24.92
10.	2-NO_2	247-49	76	N, 25.45	25.40
11.	3-NO_2	253	71	N, 25.45	25.53
12.	4-NO_2	310	70	N, 25.25	25.58
13.	2,5-$(Cl)_2$	303^d	63	Cl, 23.74	22.48
14.	2,5-$(Br)_2$	300^d	65	Br, 41.24	41.09

d—melts with decomposition.

TABLE 3—CHARACTERISTICS OF 5-ARYLAZO-4,6-DIMETHYL-2-HYDROXYPYRIMIDINES (III)

Sl. No.	X, Y	m.p. °C	Yield %	Analysis% Calcd.	Found
1.	H	239	70	N, 24.57	24.63
2.	2-CH_3	257^d	51	N, 23.14	23.28
3.	4-CH_3	242	55	N, 23.14	22.98
4.	2-OCH_3	258^d	48	N, 21.71	21.56
5	4-OCH_3	288	57	N, 21.71	21.77
6.	2-OC_2H_5	318^d	55	N, 20.58	20.79
7.	2-Cl	230	65	Cl, 13.36	13.15
8.	3-Cl	210	72	Cl, 13.36	13.15
9.	4-Br	287	68	Br, 26.05	26.17
10.	2-NO_2	298	70	N, 26.52	26.68
11.	3-NO_2	304	78	N, 26.52	26.37
12.	4-NO_2	308^d	69	N, 26.52	26.60
13.	2,5-$(Br)_2$	308^d	77	Br, 41.45	41.80
14.	2,5-$(Cl)_2$	284^d	79	Cl. 23.84	23.85

d—melts with decomposition.

Method for reduction : A solution of I (X=Y=H) (2.29 g ; 0.01 g mole) in acetic acid (20 ml) was added to a suspension of pure zinc (1.31 g ; 0.02 g atom) in water (10-15 ml) slowly and with constant stirring. The mixture was first stirred at room temperature for 30-40 min and then heated on boiling water bath for 2-3 hr. The reaction mixture was filtered and the residue washed twice with water. Combined filtrate was neutralized with dilute $NaHCO_3$ and solid separated was crystallized from ethanol to give crystals, m.p. 285° (d), (yield 51%) which was identified as 2,5-diamino-4-hydroxy-6-methylpyrimidine [lit. m.p.[5] 281-2° (d)]. (Found : N, 40.3. Calcd. for $C_5H_8N_4O$; N, 40.01%).

Similarly II (X=Y=H) and III (X=Y=H) were reduced and characterised by m.p. and elemental analysis.

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Search for New Hypoglycemic Agents. Part—VII : Coumarinylsulphonyl Ureas, Semicarbazides and Semicarbazones

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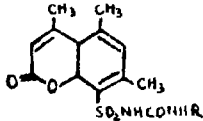
SULPHONYLUREAS[1,2,3] have long been known in the therapy of diabetes. It has recently been reported that sulphonamido coumarins[4] possess antidiabetic activity comparable to that of chlorpropamide. Moreover, some sulphonyl semicarbazides[4] and semicarbazones have also exhibited marked hypoglycemic activity. Hence, the title compounds were prepared with a view to study their hypoglycemic efficacy.

4,5,7-Trimethylcoumarin on chlorosulphonation gave 4,5,7-trimethyl-8-coumarinylsulphonyl chloride, which on treatment with ammonia was converted to the corresponding sulphonamide. The latter was allowed to react with ethyl chloroformate in the presence of anhydrous K_2CO_3 and dry acetone to yield ethyl N-(4,5,7-trimethyl-8-coumarinylsulphonyl) carbamate. The carbamate on condensation with various amines and hydrazines gave coumarinylsulphonyl ureas and coumarinylsulphonyl semicarbazides, respectively. Also, the treatment of the carbamate with hydrazine hydrate afforded a semicarbazide which was condensed with different aldehydes or ketones to furnish coumarinylsulphonyl semicarbazones.

Experimental

All melting points are uncorrected. The structures of compounds were confirmed by ir spectra and elemental analysis.

4,5,7-Trimethylcoumarin : It was prepared by the modification of the method reported earlier[6]. Polyphosphoric acid (174.5 g) was added to a solution of 3,5-dimethylphenyl (12.0 g ; 0.1 mole) in ethylacetoacetate (12.7 ml). The resulting mixture was heated at 75-80° with stirring for 20 min and thereafter poured into ice cold water. A pale yellow solid, thus obtained crystallised from dilute ethanol, yield 40%, m.p. 175-176° (lit.[7] m.p. 176°).

4,5,7-Trimethyl-8-coumarinylsulphonyl chloride : 4,5,7-Trimethylcoumarin (18.8 g ; 0.1 mol) was kept in a freezing mixture (8°) and chlorosulphonic acid (23.3 ml ; 0.2 mol) was added to it dropwise. The resulting mixture was stirred for 30 min at room temp. It was subsequently heated on a water bath at 80° for a few min and then poured into crushed ice. The product crystallised from ethanol, m.p. 177-178°, yield 60%. (Found : C, 50.00 ; H, 3.44. Calcd. for $C_{12}H_{11}O_4SCl$; C, 50.26 ; H, 3.84%).

4,5,7-Trimethyl-8-coumarinylsulphonamide : 4,5,7-Trimethyl-8-coumarinylsulphonyl chloride (0.01 mol) was treated with an excess of aq. ammonia. The resulting mixture was heated on a water bath for a few min. The product obtained on addition of water to the mixture crystallised from water, m.p. 185°, yield 80%. (Found : N, 4.95. Calcd. for $C_{12}H_{13}O_4NS$; N, 5.24%). NMR ($CDCl_3$) : δ (ppm) 1.25-1.32 (6H, d, 2 CH_3), 1.20 (3H, s, CH_3), 6.2 (1H, s, H_3), 7.4 (1H, s, H_6) and 4.5-4.6 (2H, broad hump, NH_2).

Ethyl N-(4,5,7-trimethyl-8-coumarinylsulphonyl) carbamate : A mixture of 4,5,7-trimethyl-8-coumarinylsulphonamide (21.2 g), anhydrous K_2CO_3 (27.6 g) and dry acetone (25 ml) was refluxed on a water bath for 1 hr. Thereafter, ethyl chloroformate (23.6) was added to the refluxing mixture over 1-5 hr. It was further refluxed for 3 hr and then evaporated to dryness. The residue obtained was dissolved in 150 ml of water and 1 *N* HCl was added to the solution till *p*H 8-8.5 was attained. After standing overnight, the solution was filtered and the filtrate acidified with 5 *N* HCl to attain *p*H 4, when a precipitate was obtained. It was filtered and recrystallised from ethanol, m.p. 178°. (Found : N, 3.65. Calcd. for $C_{15}H_{17}O_6NS$; N, 4.13%).

N^1-(4,5,7-Trimethyl-8-coumarinylsulphonyl)-N^3-aryl/alkyl ureas : Ethyl N-(4,5,7-trimethyl-8-coumarinylsulphonyl) carbamate (0.003 mole) and an appropriate amine (0.003 mole) were refluxed in anhydrous toluene or benzene (10 ml) for 4 hr on a water bath. A solid was obtained on cooling which crystallised from ethanol or methanol.

Melting points and pertinent data of the compounds thus prepared are recorded in Table 1.

N^1-(Phenyl/p-tolyl)-N^4-(4,5,7-trimethyl-8-coumarinylsulphonyl) semicarbazides : These were prepared analogously from ethyl N-(4,5,7-trimethyl-8-coumarinylsulphonyl)carbamate and phenyl/*p*-tolyl hydrazine. The two semicarbazides thus obtained are :

TABLE 1—N^1-[(4,5,7-TRIMETHYL-8-COUMARINYL-SULPHONYL)]-N^3-ALKYL/ARYL UREAS

Sl. No.	R	m.p. °C	Yield %	%N Found (Calcd.)	Reduction in Blood sugar in rats %
1.*	*p*-$CH_3C_6H_4$	182	88	6.55 (7.00)	15
2.*	C_6H_5	205	90	6.88 (7.25)	8
3.*	C_2H_5	181-183	80	7.94 (8.28)	8
4.*	*n*-C_4H_9	174	90	7.99 (8.88)	10
5.	*o*-$CH_3C_6H_4$	178	70	6.75 (7.00)	10
6.	*p*-$CH_3OC_6H_4$	180	60	6.83 (6.78)	0
7.	*o*-$CH_3OC_6H_4$	185	65	6.30 (6.73)	—
8.	*p*-ClC_6H_4	194	80	6.25 (6.66)	13
9.	2,4-$Cl_2C_6H_3$	180	85	5.47 (6.17)	—
10.	C_6H_{11}	188	70	6.50 (7.14)	10
11.	*p*-$O_2NC_6H_4$	179-181	60	9.41 (9.72)	—
12.	2,4-$(O_2N)_2C_6H_3$	189	40	9.34 (9.70)	—
13	2,3-$Br_2C_6H_3$	188	50	5.14 (5.55)	—
14.*	*p*-BrC_6H_4	190	50	5.71 (6.00)	—

* Showed IR spectral bands at 1190 cm^{-1} (sec SO_2NH-), 1700 cm^{-1} (C=O) and 3250 cm^{-1} ($-NH$).

I. *N^1-(Phenyl)-N^4-(4,5,7-trimethyl-8-coumarinylsulphonyl) semicarbazide*, m.p. 200°, yield 50%. (Found : N, 10.00. Calcd. for $C_{19}H_{19}O_5N_3S$; N, 10.4%). IR frequencies (cm^{-1}) : 1700 (C=O), 1200 (sec SO_2NH-) and 3200-3340 ($-NH-NH-$).

It caused reduction in blood sugar in rats by 5%.

II. *N^1-(p-Tolyl)-N^4-(4,5,7-trimethyl-8-coumarinylsulphonyl) semicarbazide*, m.p. 191°, yield 55%. (Found : N, 9.84. Calcd. for $C_{20}H_{21}O_5N_3S$; N, 10.12%). IR frequencies (cm^{-1}) : 1700 (C=O), 1160-1180 (sec SO_2NH-) and 3100-3400 ($-NH-NH-$).

It reduced the blood sugar in rats by 11%.

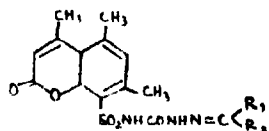
N^4-(4,5,7-Trimethyl-8-coumarinylsulphonyl) semicarbazide : A mixture of ethyl N-(4,5,7-trimethyl-8-coumarinylsulphonyl) carbamate (0.03 mol) and hydrazine hydrate (100% ; 0.035 mole) was refluxed in absolute ethanol (25 ml) for 8 hr. The product crystallised from ethanol, m.p. 165°, yield 60%. (Found : N, 12.52. Calcd. for $C_{13}H_{15}O_5N_3S$; N, 12.92%).

TABLE 3—GROSS CNS OBSERVATIONS AND ALD_{50} OF SOME COMPOUNDS

Compd. No.	Gross CNS observations										ALD_{50} mg/kg i.p.
	Dose 464 mg/kg i.p					Dose 1000 mg/kg i.p.					
	S.M.A.	Reactivity	Death	Writhing	Other effects	S.M.A.	Reactivity	Death	Writhing	Other effects	
1.	↓	↓	0/4	(+)	(–)	↓	↓	0/4	(+)	Respiration	1000
2.	↓	↓	0/4	(+)	Respiration	↓	↓	2/4	(+)	(–)	1000
3.	↓	↓	0/4	(+)	"	↓	↓	0/4	(–)	Respiration	1000
4.	↓	↓	0/4	(–)	(–)	↓	↓	0/4	(–)	(–)	650
14.	↓	↓	0/4	(–)	(–)	↓	↓	0/4	(–)	(–)	1000
17.	↓	↓	2/4	(+)	Respiration	↓	↓	0/4	(+)	(–)	870
18	↑	↑	0/4	(+)	(–)	↑	↑	0/4	(+)	(–)	1000
19.	↑	↑	0/4	(+)	Respiration	↑	↑	0/4	(+)	Respiration	1000
21.	↑	↑	0/4	(–)	Respiration	↑	↑	0/4	(–)	"	1000
22.	↑	↑	0/4	(–)	(–)	↑	↑	0/4	(–)	(–)	1000

↓ = decreased, ↑ = increased, (+) = present; (–) = not affected.
* Correspond to Tables 1 and 2.

TABLE 2—N^4-(4,5,7-TRIMETHYL-8-COUMARINYL-SULPHONYL) SEMICARBAZONES

CH_3 CH_3 CH_3 $SO_2NHCONHN{=}C<^{R_1}_{R_2}$

Sl. No.†	R^1	R^2	m.p. °C	Yield %	%N Found (Calcd.)
15.*	C_6H_5	H	180	65	9.64 (10.17)
16.*	o-ClC_6H_4	H	180	50	9.00 (9.39)
17.	$C_6H_5CH{=}CH$	H	146	50	9.41 (9.83)
18.	p-$NH_2C_6H_4$	CH_3	182	75	12.36 (12.67)
19.	p-OHC_6H_4	CH_3	176	40	9.32 (9.74)
20.	C_6H_5	CH_3	120	95	9.46 (9.88)
21.*	C_6H_5	C_6H_5	152	50	8.14 (8.58)
22.	C_5H_{10}		175	50	10.31 (10.37)

* Showed ir spectral bands at 1200 cm^{-1}(sec SO_2NH-), 1700 cm^{-1}(C=O), 3100-3400 cm^{-1}(–NH) and 1600-1660 cm^{-1}(–N=C–).

† Correspond to those in Table-1.

N^4-(4,5,7-Trimethyl-8-coumarinylsulphonyl) semicarbazones : Equimolar amounts of N_4-(4,5,7-trimethyl-8-coumarinylsulphonyl) semicarbazide and an aldehyde/ketone were refluxed in absolute ethanol in the presence of a drop of glacial acetic acid for 4 hr. The product crystallised from ethanol.

Analysis, melting points and yield of the prepared semicarbazones are presented in Table 2.

Bioassay :

(a) *Hypoglycemic activity :* The two compounds (I and II above) and eight compounds (Table 1) were tested for hypoglycemic activity. They showed very little activity.

(b) *CNS activity :* For studying their action on the central nervous system (CNS), the compounds were administered to albino mice in different doses and their behavioural changes in spontaneous motor activity and reactivity to sound and touch were noted. Ten compounds (Table 3) were screened for CNS activity. They showed very little CNS depressant or stimulant activity.

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Studies on Some Biologically Active Quinazolones Synthesis of 2-phenoxy methyl-3-N-substituted Amino Carbonyl methyl-8-substituted 4(3H) quinazolones as Anticonvulsant Agents

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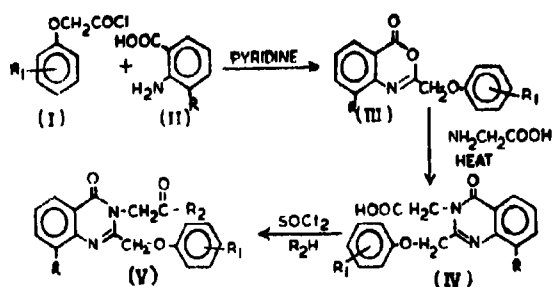
QUINAZOLONES and their derivatives have drawn attention because of their prodigious range of activity e. g., CNS depressant[1], hypnotic[2], anticonvulsant[3,4], M.A.O. inhibitory[5], etc. In the present paper we have described the synthesis of newer quinazolone derivatives with a view of getting enhanced anticonvulsant activity.

Substituted 4H-3,1 benzoxazines[6] (III) were synthesised by the cyclization of substituted phenoxy acetyl chlorides[7] with substituted anthranilic acids in pyridine. The compound III on condensation with glycine gave 2-phenoxymethyl-3-carboxymethyl-8-substituted 4(3H) quinazolones (IV). Acid chloride of (IV) on condensation with different amines in dry benzene and pyridine gave the desired product 2-phenoxymethyl-3-N substituted amino carbonyl methyl-8-substituted 4(3H) quinazolones (V).

Scheme I

Experimental

Melting points were taken in open capillary and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 137 spectrophotometer in KBr.

2-(o-Methyl phenoxy methyl)-3-carboxymethyl-8-iodo-(3H)-4-quinazolones : 2-(*o*-Methyl phenoxy methyl)-8-iodo anthranil (3.93 g ; 0.01 mole) and glycine (0.8 g ; 0.01 mole) were taken in 2 : 1 pyridine water mixture (30 ml) and refluxed on wire gauge for 5-6 hr. The solvent was distilled under reduced pressure. The residue was digested with 4 *N* HCl (100 ml) on a steam bath for 2-3 hr. The solid mass thus separated was filtered and crystallised from ethanol, m.p. 257°, yield 2.69 g (57%). IR (KBr) ν_{max} cm^{-1} : 1695 (COOH), 1230 (C–O–C), 1660 (N–C=O) and 1610 (C=N). Anal. Found : C, 47.64 ; H, 3.13 ; N, 6.01. $C_{18}H_{15}N_2O_4I$ requires C, 48 ; H, 3,3 ; N, 6.02%. Other compounds of this series were similarly prepared and the results are recorded in Table 1.

TABLE 1—PHYSICAL DATA OF 2-(SUBSTITUTED)PHENOXY METHYL-3-CARBOXYMETHYL-8-SUBSTITUTED-4-QUINAZOLONE (IV)

Comp.* No.	R	R_1	m.p. °C	Molecular formula
Ia	H	H	209	$C_{17}H_{14}N_2O_4$
Ib	H	*o*-Cl	218	$C_{17}H_{13}O_4Cl$
Ic	H	*o*-OCH_3	221	$C_{18}H_{16}N_2O_4$
Id	H	*p*-CH_3	199	$C_{18}H_{16}N_2O_4$
Ie	I	H	248	$C_{18}H_{15}N_2O_4I$

* The compounds were obtained in about 66-70% yields. Elemental analyses of C, H and N were consistent.

2-(o-Methyl phenoxy methyl)-3-N-morpholinyl carbonyl methyl-8-iodo-4(3H)-quinazolone : A mixture of IV (2.25 g ; 0.005 mole) and thionyl chloride (1.19 g ; 0.01 mole) was refluxed in dry benzene (35 ml) for 5-6 hr. Excess of benzene was distilled under reduced pressure and morpholine (0.48 g ; 0.005 mole) in pyridine (30 ml) added to the reaction mixture. The solution was refluxed for 2 hr. Excess of pyridine was removed and the residue poured in dil HCl and kept overnight. The solid thus separated was crystallised from ethanol to give V, m.p. 162°, yield 1.36 g (50%). Anal. Found : C, 50.52 ; H, 3.91 ; N, 8.01%. $C_{22}H_{21}N_3O_4I$ requires C, 50.91 ; H, 4.054 ; N, 8.108%. IR (KBr) ν_{max} cm^{-1} : 1630 (CON<), 1670 (C–N). NMR ($CDCl_3$) δ : 7.77 (d, 1H, J=8Hz, C_5–H), 7.31 (t, 1H, J=8Hz, C_6–H), 6.92 (d, 1H, J=8Hz. C_7–H), 8.12 (d, 1H, J=7Hz, C_3–H), 7.64-6.82 (m, 2H, $C_{3'-6}$ –H), 7.81 (d, 1H, J=7Hz, $C_{3'}$ –H), 2.5 (s, 3H, CH_3), 3.88 (t, 2H, J=6Hz, OCH_2).

Other compounds of the series were prepared similarly and the results are shown in Table 2.

Biological activity : The compounds were administered i.p. in albino mice of either sex in different doses and approximate LD_{50} values were determined by conventional procedure[8]. The results given in Table 2 indicate that the compounds were relatively nontoxic because their LD_{50} values are quite high.

The anticonvulsant activity of V against pentylene tetrazole induced seizures was determined in mice[9]. The protection ability against pentylene tetrazol induced seizures ranged from 20-70% (Table 2). Maximum protection was observed in compound II_e and minimum protection in compound II_f. These results possibly indicate that the introduction of nucleophile in phenyl ring at position 2 reduced its protecting ability, while introduction of electrophile enhanced its activity.

TABLE 2—PHYSICAL DATA AND BIOLOGICAL ACTIVITY OF 2-PHENOXYMETHYL-3-N-SUBSTITUTED AMINO CARBONYL METHYL-8-SUBSTITUTED-4(3)-QUINAZOLONE (V)

Compound* No.	R	R_1	R_2	m.p. °C	Molecular formula	LD_{50}	Anticonvulsant activity	
							Protection (%)	Mortality (%)
IIa	H	H	morpholinyl	110-112	$C_{21}H_{21}N_3O_4$	1000	60	60
IIb	H	o-Cl	thiazolyl	139-140	$C_{20}H_{18}N_4O_3SCl$	1000	80	80
IIc	H	o-Cl	pyrrolidinyl	128-130	$C_{21}H_{20}N_3O_3Cl$	900	40	60
IId	H	H	pyrrolidinyl	120-121	$C_{21}H_{21}N_3O_3$	980	50	50
IIe	H	o-Cl	cyclohexyl	145	$C_{23}H_{24}N_3O_3Cl$	1000	80	70
IIf	H	o-Cl	piperidinyl	105-107	$C_{22}H_{22}N_3O_3Cl$	850	20	80
IIg	H	o-CH_3	thiazolyl	150-151	$C_{21}H_{18}N_4O_3S$	1000	60	40
IIh	H	H	thiazolyl	198-200	$C_{20}H_{16}N_4O_4S_2$	950	50	40
IIi	H	H	cyclohexyl	182	$C_{23}H_{25}N_3O_3$	1000	40	60
IIj	H	o-CH_3	morpholinyl	201	$C_{22}H_{23}N_3O_4$	1000	60	40
IIk	I	H	thiazolyl	215	$C_{20}H_{15}N_4O_3SI$	980	50	40
IIl	H	o-CH_3	piperidinyl	135	$C_{23}H_{25}N_3O_3$	1000	30	70
IIm	H	H	piperidinyl	170	$C_{22}H_{23}N_3O_3$	900	40	50
IIn	I	H	morpholinyl	140	$C_{21}H_{20}N_3O_4I$	850	50	40

* The compounds were obtained in about 60-64% yields.
Elemental analysis of C, H and N were obtained within ±0.4%.

IIb NMR ($CDCl_3$) δppm, 8.33 (d, 1H, J=7Hz, C_5−H), 7.63-6.85 (m, 2H, C_{6-7}−H), 7.83 (d, 1H, J=7Hz, C_8−H), 8.25 (d, 1H, J=7Hz, $C_{3'}$−H), 7.60-6.82 (m, 2H, $C_{3'-4'}$−H), 7.80 (d, 1H, J=7Hz, $C_{6'}$−H), 3.88 (t, 2H, J=6Hz, OCH_2).

IIg. 8.30 (d, 1H, J=7Hz, C_5−H), 7.61-6.81 (m, 2H, C_{6-7}−H), 7.83 (d, 1H, J=7Hz, C_8−H), 8.19 (d, 1H, $C_{3'}$−H), 7.64-6.82 (m, 2H, $C_{3'-4'}$−H), 7.80 (d, 1H, J=7Hz, $C_{6'}$−H), 2.5 (s, 3H, CH_3), 3.88 (t, 2H, J=6Hz, OCH_2).

IIi. 8.83 (d, 1H, J=7Hz, C_5−H), 7.61-82 (m, 2H, C_{6-7}−H), 7.81 (d, 1H, J=7Hz, C_8−H), 2.72 (m, 5H, Arom) 3.88 (t, 2H, J=6Hz, OCH_2).

IIr. 7.76 (d, 1H, J=8Hz, C_5−H), 7.32 (t, 1H, J=8Hz, C_6−H), 6.93 (d, 1H, J=8Hz, C_7−H), 2.70 (m, 5H, Arom), 3.82 (t, 2H, J=6Hz, OCH_2).

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Synthesis of 1,2,4-Oxadiazolines Having Antifungal Activity

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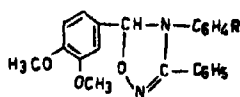
IN continuation of our work on the synthesis of new heterocyclic compounds[1,2] having antifungal activity 1,2,4,-oxadiazolines have been prepared by the cycloaddition of benzonitrile oxide to 3,4-dimethoxybenzalanilines[3]. The cycloaddition of benzonitrile oxide to 3,4-dimethoxybenzalanilines has been carried out at 0° using different solvents like ether, chloroform, etc. depending upon the solubility of the Schiff bases. Benzonitrile oxide was generated *in situ* by the reaction of bases like triethylamine or 14% sodium hydroxide on the hydroxamoyl chloride[3]. A mixture of two products was obtained in each case. The major product has been found to be the cycloadduct (I) and the minor one is identified as dimer[4] (II) of the nitrile oxide through its m.p. and m.m.p. The cycloadducts can have a structure either Ia or Ib.

(Ia) (Ib)

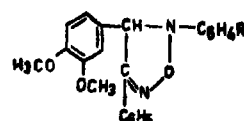



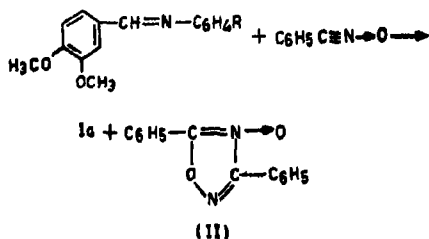
TABLE 1

Sl. No.	R	m.p. °C	Molecular formula	N% Found (Calcd.)
1.	H	65	$C_{23}H_{20}N_2O_3$	7.75 (7.77)
2.	p-CH_3	81	$C_{24}H_{22}N_2O_3$	7.52 (7.49)
3.	m-Cl	67	$C_{23}H_{19}N_2O_3Cl$	7.09 (7.10)
4.	p-Cl	74	$C_{23}H_{19}N_2O_3Cl$	7.09 (7.10)
5.	p-Br	89	$C_{23}H_{19}N_2O_3Br$	6.39 (6.38)

The infrared spectrum of the cycloadduct showed bands at 1680 cm^{-1}(–CH=N–). NMR spectrum in $CDCl_3$ of the cycloadduct (I, R=H) showed six methoxy protons at 6.1 τ, 13 aromatic protons at 2.7 τ and one proton on the C_5 of the oxadiazoline ring at 2.1 τ. Such a low field shift of C_5 proton supported sturucture Ia rather than Ib in which proton is deshielded only by a nitrogen atom.

H_3CO, OCH_3 –CH=N–C_6H_4R + $C_6H_5C{\equiv}N{\to}O$ ⟶

Ia + C_6H_5–C=N→O ... C_6H_5

(II)

These 1,2,4-oxadiazolines (1 to 5) were tested for their antifungal activity against *Puccinia striformis*, *Puccinia recondita*, *Alternaria triticina*, *Alternaria tenuis* and *Pestalotia psidii* by employing standard method of spore germination inhibition. Three concentrations, viz., 1000, 500 and 250 ppm of each of the compounds, have been tried against all the test fungi. All the compounds possessed promising antifungal activity against the above fungi and caused 100% spore germination inhibition even at 250 ppm. The study at still lower concentration is in progress. These observations confirmed our earlier results that presence of methoxy phenyl ring in a compound helps in increasing its activity[1].

Experimental

1,2,4-Oxadiazoline (I, R=H) : 3,4-Dimethoxybenzalaniline (2.41 g ; 0.01 mole) was dissolved in ether (100 ml) and cooled in an ice bath to 0°. Benzhydroxamoyl chloride (1.1 g ; 0.01 mole) in ether (20 ml) was then added with constant shaking and the contents were kept at 0° for some time. Triethylamine (1.2 ml) in ether (20 ml) was then added at a very slow rate with continuous shaking. When the addition was complete the reaction mixture was allowed to stand at 0° for 2 hr. The ether layer was separated out and the residue was washed thrice with dry ether. The combined ether layer and the washings on evaporation of the solvent yielded crystalline solid which on recystallization from benzene-petroleum ether mixture gave fine shining crystals, m.p. 65° (yield 85%).

Testing of the compounds against fungus : Three concentrations (250, 500 and 1000 ppm) of I (R=H) were taken and treated against fungus *Puccinia striformis*. The treated spores were incubated for 18 hr and percent spore germination inhibition was calculated by counting 200 spores of each treatment. Spores incubated in water + respective solvent in which the compound is dissolved were used as control. The following formula is used to calculate % spore germination inhibition.

$$\%\ \text{Spore germination inhibition} = \frac{\text{Spore germination inhibition} - \text{Control}}{\text{Control}} \times 100$$

Similary, other 1.2,4-oxadiazolines were tested for their antifungal activity against *Puccinia striformis* and other fungi viz , *Puccinia recondita*, *Alternaria triticina*, *Alternaria tenuis* and *Pestalotia psidii*.

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Chemical Examination of *Medicago sativa* Seeds

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MEDICAGO sativa[1-3](Leguminosae), known as alfalfa or lucerne, is an erect, much branched annual herb. Its seeds are yellowish brown in colour, kidney shaped, rich in vitamin and enzyme. Looking to its nutritive value, it was thought interesting to investigate fixed oil and unsaponifiable matter from the seeds of this plant.

The crushed seeds of *Medicago sativa* were exhaustively extracted with pet. ether (60-80°) and a yellowish brown coloured fixed oil (yield 8.50%) was obtained. The oil was found to have following physico-chemical values.

Specific gravity (25%)	0.9275
Refractive index .	1.4624
Acid value	5.32
Saponification value ...	178.56
Iodine value ..	8.26
Acetyl value	99.50

100 g of the oil was saponified[4] and the mixed acids (88 g) obtained. The mixed acids were resolved into saturated (7.5 g) and unsaturated (41.5 g) fractions.

Paper and thin layer chromatographic studies showed the presence of palmitic, oleic, linoleic, linolenic and stearic acids.

The fatty acid methyl esters were analysed by gas liquid chromatography using a column of Rheoplex 400-15% supported by chrom-W acid

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washed of S.S. 4.5′ XI/B.O.D. maintained at 180°. Injection port and detector block were maintained at 270° with a flow rate of 40 ml/min with a chart speed of 15 mm/min.

The percentage composition of the acids were calculated based on peak areas[5] and it was found to be composed of palmitic (18.10%), oleic (17.60%), linoleic (60.60%), linolenic (2.20%) and small amount of stearic acids.

Chromatographic resolution of the unsaponifiable matter resulted in the isolation of β-amyrin, m.p. 197-98° and β-sitosterol, m.p. 136-37° which were identified by direct comparison with authentic samples.

Acknowledgement

One of the authors (S. P. S.) is grateful to Prof. S. S. Nigam for providing authentic samples of β-amyrin and β-sitosterol.

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Chemical Constituents of *Cephalotaxus griffithii*

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CEPHALOTAXUS griffithii HK (Fam. Cephalotaxaceae), collected from Nainital, has been investigated for its chemical constituents and led to the isolation of amentoflavone, sequoiaflavone, apigenin, ginkgetin, mono-O-methyl-C-methyl amentoflavone and quercitrin. 1,6-C-Methyl-1,7-O-methyl amentoflavone constitutes the second report of isolation and characterization of naturally occurring C-methyl biflavones.

Finely ground dried leaves of *Cephalotaxus griffithii* (3 kg) were successively extracted with petrol (40-60°), benzene, chloroform, ethyl acetate and finally with acetone. The last two extracts were concentrated and chromatographed over silicagel to furnish six bands labelled as CGI, CGII, CGIII, CGIV, CGV and CGVI, in order of increasing R_f values. All these bands were separated by preparative tlc (BPF, 36 : 9 : 5)[1] and eluted by acetone mixed with pyridine (2%). CCI (0.2 g) obtained, gave a single spot on tlc, R_f 0.18, m.p. 320°. The yellow solid mass (80 mg) was methylated to give hexa-O-methyl amentoflavone (50 mg), m.p. 173-74°, R_f 0.40. Acetylation (Ac_2O/pyridine) of yellow solid (80 mg) yielded a white solid which crystallized from $CHCl_3$-MeOH to give amentoflavone hexaacetate, m.p. 242-43°.

The identity of sequoiaflavone and apigenin was established by direct comparison of their acetate and methylethers with those of authentic samples. (m.p., m.m.p., flourescence in uv light and nmr data).

CGIV, m.p. 350° (decom), $C_{30}H_{16}O_8(OMe)_2$, λ_{max} (ethanol) : 271 nm band I, 335 nm band II. Tetraacetyl derivative, $C_{30}H_{12}O_4(OMe)_2$, $(OAC)_4$, was prepared, m.p., 265-267°. λ_{max} (ethanol) : 211, 248-258, 317 nm, finally confirmed as dimethylether of amentoflavone (ginkgetin) by comparison with an authentic sample.

CGV, m.p. above 338°, R_f 0.39, $C_{32}H_{22}O_{10}$, M^+566. Mass spectrum of its methylether showed mol. ion peak at M^+636 and base peak at m/e 621, m.p. 234, R_f 0.45. The compound was finally established as 1,6-C-methyl-1,7-O-methyl amentoflavone by comparison (co.tlc, uv, nmr and mass) with authentic sample[2].

CGVI, $C_{21}H_{20}O_{11}$, λ_{max} 275, 352 m μ was hydrolysed (10% HCl) and aglycone and sugar were chromatographed with authentic samples. The sugar was found to be rhamnose. The aglycone, m.p. 182-185° was identical in all respects with quercetin. The structure of CGVI was finally confirmed as quercetin 3-rhamnoside by comparison of its nmr spectral data with that of authentic sample.

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Selective Microgram Detection of Iron(III) on Ion Exchange Resin Beads

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THE analytical importance of resin beads for the detection of inorganic and organic compounds have been well established[1-3]. The advantage of using resin spot test over detection techniques lies in the fact that it not only increases the sensitivity but also enhances the selectivity. Though a number of methods for the detection of iron(III) are available in the literature[4-6], these are either insensitive or suffer from interferences of a large number of cations specially with Fe(II) and anions. We describe in this paper a sensitive and selective method for the detection of iron(III) on resin beads in microgram of the sample.

Experimental

Reagents : All the reagents used were of analytical grade.

Test solutions : Solutions of $Fe(NO_3)_3$ (0.001 *M*) and anisaldimine antipyrine (0.5%) were prepared in distilled alcohol.

Resin : Dowex 50 W×8 (20-30 mesh) in H^+ form was used after regeneration and washing with demineralized water. The beads were soaked on a filter paper and used for the detection.

Procedure : 5-10 beads of ion-exchange resin in H^+ form were taken in a spot plate. To this one drop of anisaldimine antipyrine solution was added. Then 0.1 ml of 0.001 *M* ferric nitrate (containing 5.6 μg of Fe) was added. The *p*H was maintained around 6. The beads turned pink after 2 min. The colour of the beads was compared by a simultaneous test in the absence of iron. With the successive increment in the iron content in the solution, the colour of the beads changes from pink to violet. The lower limit of the detection for iron(III) was found to be 1.12 μg.

Interferences : To show the analytical importance of the test, the detection of iron(III) (1.12 μg) was also performed in the presence of a large number of cations and anions using the above procedure. The limit of tolerence for each ion is given in Table 1.

TABLE 1—EFFECT OF FOREIGN IONS IN THE DETECTION OF Fe(III) ; Fe(III)=1.12 μg.

Sl. No.	Foreign ions	Limit of tolerance (μg)
1.	VO_2^+	500
2.	Cr^{3+}	500
3.	Co^{2+}	500
4.	Ni^{2+}	500
5.	Cu^{2+}	500
6.	Zn^{2+}	500
7.	Zr^{4+}	500
8.	Sn^{4+}	500
9.	Bi^{3+}	500
10.	Th^{4+}	500
11.	Ce^{3+}	500
12.	Pt^{4+}	500
13.	UO_2^{2+}	500
14.	Na^+	1000
15.	K^+	1000
16.	Ca^{2+}	1000
17.	Mg^{2+}	1000
18.	Ba^{2+}	1000
19.	Sr^{2+}	1000
20.	Pb^{2+}	1000
21.	Al^{3+}	1000
22.	Cd^{2+}	1000
23.	In^{3+}	1000
24.	La^{3+}	1000
25.	Hg^{2+}	1000
26.	Ag^+	1000
27.	Y^{3+}	1000
28.	Acetate	250
29.	Molybdate	250
30.	Tungstate	250
31.	Phosphate	1000
32.	Bromate	1000
33.	Iodate	1000
34.	Chlorate	1000
35.	Sulphate	1000
36.	Chloride	1000
37.	Bromide	1000
38.	Iodide	1000
39.	Chromate	1000
40.	Vanadate	1000
41.	Fe(II)	2000

The result of the above study reveals that iron in a sample can be successfully detected upto a limit of 1.12 μg using strong exchange resin in the H^+ form in the presence of anisaldimine antipyrine as reagent. The procedure is simple and less time consuming. The advantage of using the ion exchange beads as a detection medium is that it retains the colour for a fairly long time after the test is performed. The colour starts disappearing at once when the same test is performed in the absence of beads. An additional advantages of this procedure is that it distinguishes between Fe(III) and Fe(II) as in the latter case the test gives negative results.

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Colorimetric Estimation of Ce(IV) by Phenothiazines

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SANKE Gowda and others[1] have reported a method of estimation of Ce(IV) by using fluphenazine hydrochloride as a complexing reagent. Our present investigation relates to the use of different phenothiazines as reagents for the spectrophotometric estimation of Ce(IV).

Experimental

Standard solution of Ce(IV) (100 ppm) was prepared by dissolving requisite amount of ammonium ceric nitrate in distilled water and was standardised by the method given in literature[2]. 1% solutions of phenothiazines in methanol were prepared and used as reagents

Procedure : To a solution containing 100 μg of cerium(IV) is added 0.5 ml of 1% ligand solution and mixed. The acidity of the mixture is adjusted between 2.4 to 4.0 molar with orthophosphoric acid in a total volume of 10 ml. The solution is diluted to 10 ml with distilled water and absorbance of the solution is recorded after 5 min at 510 nm. The amount of metal present in the solution is then determined from the calibration curve drawn under identical conditions.

The colour of the complex attains stability 5 min after the addition of reagent and is stable upto 25 min.

Physico chemical constants of the complexes have been summarised in Table 1. Molar composition of the complexes were determined by Job's method of continuous variation[3] and were found to be 1 : 1 (M . L) in all the cases.

TABLE 1

Sl. No.	Reagent	Operative range from Ringbom's plot . μg/ml	Molar absorptivity $\times 10^{-3}$ lit. mole^{-1}cm^{-1}	Sandell's sensitivity μg/cm^2
1.	Promethazine HCl	3.6 to 12.9	4.48	3.1×10^{-2}
2.	Promazine HCl	5.6 to 12.9	5.61	2.5×10^{-2}
3.	Chlorpromazine	4.0 to 14.1	6.73	$2 1\times10^{-2}$
4.	Thiopropyrazine mesylate	4.7 to 15.8	6.45	2.2×10^{-2}

The tolerance limits of various cations and anions are : Cd^{2+} (1 : 10) ; Ni^{2+} (1 : 8) ; Zr^{2+} (1 : 10) ; Cu^{2+} (1 : 10) ; Pb^{2+} (1 : 10) ; Fe^{3+} (1. 10); U^{6+} (1 : 10) ; Mn^{2+} (1 : 10) ; Be^{2+} (1 : 10) ; Th^{4+} (1 : 10) ; Zn^{2+} (1 : 10) ; Ca^{2+} (1 : 10); Ba^{2+} (1:10); Cl^- (1 : 10) ; Br^- (1 : 10) ; SO_4^{2-} (1 : 10) ; NO_3^- (1 : 10) ; CH_3COO^- (1 : 10) ; ClO_3^- (1 : 8) ; $B_4O_7^{2-}$ (1 : 10) ; MoO_4^{2-} (1 : 6) ; $C_2O_4^{2-}$ (1 : 10).

It was found that cations such as Sn^{2+}, Fe^{2+}, As^{3+}, V^{5+} and anions such as NO_2^-, $Fe(CN)_6^{4-}$, CNS^-, $S_2O_8^{2-}$, SO_3^{2-}, BrO_3^- interfere seriously with the reaction.

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Spectrophotometric Determination of Ruthenium with Prochlorperazine *Bis*methanesulphonate

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DURING the investigation on the reaction of phenothiazines with metal ions, prochlorperazine *bis*methanesulphonate, (PCPMS) 2-chloro-10-[3-(4-methyl-1-piperizinyl) propyl] phenothiazine *bis*methanesulphonate, was found to give red colour with ruthenium(III) in phosphoric, sulphuric or hydrochloric acid. This reaction is now utilized for rapid spectrophotometric determination of ruthenium(III). The proposed method offers the advantages of simplicity, rapidity, sensitivity, reasonable selectivity and determination at room temperature without the need for extraction.

Experimental

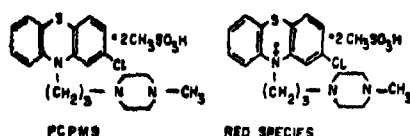
Reagents and apparatus : A stock solution of ruthenium(III) was prepared by dissolving ruthenium(III) chloride (Johnson and Matthey, London) in dilute hydrochloric acid and diluting to 1 litre to give a solution of 1 *M* with respect to hydrochloric acid. The solution was standardized gravimetrically[1] and was further diluted to give a solution of 25 μg/ml. A 0.2% solution of PCPMS was prepared in double distilled water and stored in an amber bottle in a refrigerator. A Beckman Model DB spectrophotometer with matched 1 cm silica cells was used for absorbance measurements.

Procedure : An aliquot of the stock solution containing 5-205 μg of ruthenium(III) and 14 ml of 10 *M* phosphoric acid were transferred to a 25 ml volumetric flask, 3 ml of 0 2% PCPMS solution was added to this and the volume made upto the mark with double distilled water. The solutions were

mixed well and the absorbance was measured at 529 nm against the corresponding reagent blank prepared in the same manner. The amount of ruthenium in the sample solution was deduced from the standard calibration curve.

Results and Discussion

PCPMS readily forms red species with ruthenium(III) at room temperature (27°) in phosphoric, sulphuric or hydrochloric acid. The study of the red species, which is believed to be a radical cation[2,3], in sulphuric and hydrochloric acid media is not recommended because the reaction is less sensitive, less stable and many foreign ions interfere. Phosphoric acid was therefore selected for further studies. PCPMS and red species have the following structure.

PCPMS ($\cdot 2CH_3SO_3H$) RED SPECIES ($\cdot 2CH_3SO_3H$)

The effect of varying the concentration of phosphoric acid was investigated. The rate of colour development and the sensitivity increase with increasing acid concentration from 0.5-5 M and then remain constant over the range 5-6 M (Fig. 1). The maximum colour development takes place instantaneously at room temperature in 5-6 M acid. An acid strength of 5.5 M of H_3PO_4 was chosen for all subsequent work. The absorbance of the red species remains constant for 90 min.

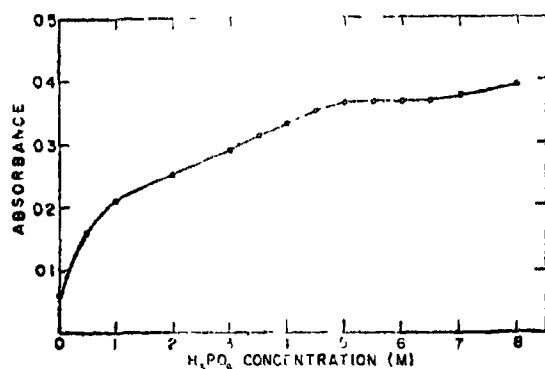



Fig. 1. Effect of H_3PO_4 concentration.

The absorption spectra of the reagent, ruthenium(III) and the red species in 5.5 M phosphoric acid are shown in Fig. 2. The red species exhibits maximum absorbance at 528-530 nm. The reagent and ruthenium(III) show little absorption at this wave length. Subsequent studies were made at 529 nm.

Beer's law was obeyed over the concentration range 0.2-7.3 ppm of ruthenium(III) with an optimum concentration range 0.7-6.9 ppm. The molar absorptivity was 1.17×10^4 l. mol^{-1} cm^{-1}. Sandell's

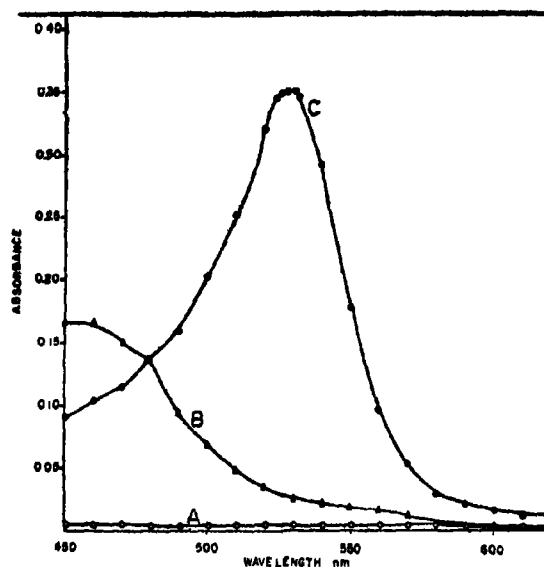



Fig. 2 Absorption spectra of reagent blank, ruthenium(III) and red species.

A. Reagent blank, B. Ruthenium(III) and C. Red species [Ru(III) = 3 ppm, H_3PO_4 = 5.5 M].

sensitivity was estimated to be 8.6 ng cm^{-2}. The standard deviation calculated from 10 determinations on a solution containing 3 ppm of ruthenium was ±0.025.

The effect of reagent concentration was examined by measuring the absorbance of solutions containing 3 ppm of ruthenium(III) and varying amounts of PCPMS. A 12-fold molar excess of the reagent was necessary to produce maximum colour intensity. The optimum amount of 3 ml of 0.2% of the reagent solution was used. There is no appreciable change in the absorbance if the order of addition of reactants is varied. The absorbance values are not affected over the temperature range 10-52°. Above

TABLE 1—EFFECT OF DIVERSE IONS IN THE DETERMINATION OF Ru(III) (AMOUNT OF Ru(III) TAKEN, 3 ppm)

Ion added	Tolerance limit* ppm	Ion added	Tolerance limit* ppm
Fe(III)	4000	Pb(II)	260
Co(II)	150	V(V)	0.1
Cu(II)	1100	W(VI)	800
Ni(II)	1000	Ti(IV)	700
U(VI)	1300	Mn(II)	600
Zn(II)	1800	Ta(V)	800
Mg(II)	2400	F^-	2800
Ag(I)	1.5	Cl^-	6000
Pd(II)	1.2	Br^-	4000
Pt(IV)	35.0	I^-	1.2
Au(III)	0.8	NO_3^-	4800
Os(VIII)	0.8	SO_4^{2-}	10000
Rh(III)	24.0	Acetate	2800
Ir(III)	18.0	Citrate	1600
Al(III)	1400	Oxalate	1500
Mo(VI)	800	EDTA	180
Zr(IV)	900	Tartrate	1600

* Amount causing an error of less than 2%.

52°, the absorbance gradually decreases with the rise in temperature.

The interference of several cations and anions which often accompany ruthenium were examined by carrying out determinations of 3 ppm of ruthenium(III) in the presence of each of these ions. Results in Table 1 show that PCPMS is selective for ruthenium(III), but Pd(II), Os(VIII), Au(III), V(V), Ag(I) and iodide interfere strongly. The nature of the red species was studied by passing an aliquot of the solution of the species through cation exchange resin, Dowex 50W−X8 and anion exchange resin Dowex 1−X8. The red species was retained by Dowex 50W−X8 and not retained by Dowex 1−X8. This indicated that the species is cationic.

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An Indirect Method for Iodometric Microdetermination of Certain Organic Acids

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SINCE most carboxylic acids are weakly dissociated, their alkalimetry at micro level is confronted with two difficulties—poor inflection on the *p*H neutralisation curve which further contracts with increasing dilution of acid and alkali, and fading away of the phenolphthalein colour at the end-point[1].

Potentiometric location of the end-point is hampered owing to the formation of a buffer[2]. The alkalimetry in non-aqueous medium has also been attempted using protophilic solvents, but in micro acidimetry the detection of the end-point is difficult. Further, titrants such as sodium triphenylmethyl and lithium aluminium hydride are too unstable to be used as 0.01 *N* standards[1].

The present communication describes a micro procedure which consists of heating the acid sample with iodide and a known excess of potassium iodate solution and subsequent iodometric determination of the surplus iodate. The quantity of acid present in the test solution is calculated from the amount of iodate consumed. The quantitative reaction is accomplished only in 3-5 min even with samples containing as low as 0.025 meq of the different organic acids studied. In order to ascertain suitable experimental conditions for the determination, the effect of change in the amount of iodide and iodate and in the reaction period in the case of each acid has also been investigated. On the basis of the results of these preliminary experiments a general procedure applicable for determining 0.025-0.1 meq of certain organic acids has been worked out.

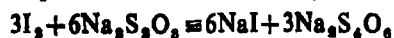
Experimental

Reagents: The following solutions were prepared using analytical grade chemicals and conductivity water, 0.1 *N* (0.0166 *M*) potassium iodate, which was also used to standardize the sodium thiosulphate solution (0.1 *N*), 0.01 and 0.005 *N* solutions were obtained by suitable dilution of the 0.1 *N* solutions. 0.05 *N* solutions of mono-, di- and tri-chloroacetic, furoic, sulphamic, *β*-chloropropionic, *iso*butyric, fumaric and benzilic acids were prepared and standardized by alkalimetry and diluted suitably to prepare the test solutions. In addition, 10% potassium iodide, 4 *N* sulphuric acid and 1% aqueous starch solutions were also prepared.

Procedure: An aliquot of an acid solution containing 0.025-0.1 meq of the acid is pipetted into a 100 ml erlenmeyer flask and 10 ml of 10% potassium iodide and 5-20 ml of 0.01 *N* potassium iodate solution (about 100% excess) are added. The flask is then kept immersed in a boiling water bath for 3-5 min after which it is cooled immediately under tap. 1 ml of starch solution is introduced and thiosulphate solution is added dropwise with constant shaking until the decolourisation of the blue colour. About 2 ml of 4 *N* sulphuric acid is them added and the liberated iodine is titrated with 0.01 or 0.005 *N* thiosulphate. A blank is also run. The difference between the blank and the experimental titres gives the amount of iodate used up. From this, the quantity of the acid present in the assay solution is calculated using the following relationships.

$$IO_3^- + 5I^- + 6H^+ \equiv 3H_2O + 3I_2$$

$$3I_2 + 6Na_2S_2O_3 \equiv 6NaI + 3Na_2S_4O_6$$

$$6COOH \equiv 6H^+ \equiv IO_3^- \equiv 3I_2 \equiv 6Na_2S_2O_3$$

1 ml of 0.01 *N* thiosulphate ≡ 0.45 mg of COOH group.

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Results and Discussion

The proposed iodometric method has been applied for the determination of certain organic acids of varied nature. The recovery studies have been performed at three different concentration levels of each acid and the results recorded in Table 1 are the average of 6 determinations. Table 1 also gives a comparative study of errors observed in the alkalimetric and the proposed method for different acids studied. The average deviation in the latter method is in the range of 0.1-0.3%.

According to Smith[3], a neutralisation indicator works satisfactorily only when the inflection or the *p*H neutralisation curve is more than 2 *p*H units. In titrating organic acids at micro level using 0.01 *N* alkali as the titrant, the inflection range is small. The difficulty in the dectection of the end-point is further accentuated by the fading away of the phenolphthalein colour at the end-point. The alkalimetry of weak acids at micro level, therefore, gives a considerable positive error[4].

TABLE 1—DETERMINATION OF CERTAIN ORGANIC ACIDS

Acid	Present mg	Alkalimetry Found mg	Alkalimetry %Average deviation	Iodometry Found mg	Iodometry %Average deviation
Acetic	6 000	6.030	+0.50	5.995	−0.08
	3.000	3.030	+1.00	3.003	+0.10
	1 500	1.527	+1 83	1 497	+0 20
Monochloroacetic	9.450	9.488	+0 40	9 458	+0 08
	4.725	4.764	+0.83	4.730	+0 10
	2.633	2.398	+1 50	2 359	-0.18
Dichloroacetic	12.900	12.943	+0.33	12.889	−0.08
	6 450	6.504	+0 84	6 461	+0 17
	3.225	2.268	+1 33	3.220	−0.15
Trichloroacetic	16.350	16.377	+0.16	16.337	−0.08
	8 175	8.216	+0 50	8 168	−0 08
	4.088	4.136	+1.17	4 091	+0 16
Furoic	11.208	11.245	+0.33	11 226	+0 16
	5.604	5 651	+0 84	5 595	−0.16
	2.802	2 844	+1 50	2.806	+0.16
Sulphamic	9 709	9.758	+0 50	9.718	+0 12
	4.855	4 887	+0 66	4.863	+0 16
	2.427	2 463	+1 50	2.423	−0.16
β-Chloropropionic	10.853	10.889	+0.33	10.836	−0.16
	5.426	5.480	+0.99	5.435	+0.16
	2 713	2 571	+1.40	2 722	+0.33
Isobutyric	8.810	8.869	+0.66	8.795	−0.16
	4.405	4.449	+1.00	4.390	−0.33
	2.203	2.240	+1.66	2 196	−0 33
Fumaric	5.803	5.822	+0.33	5.793	−0.16
	2.902	2.931	+1 00	2 897	0 16
	1.451	1.470	+1 38	1 446	−0.33
Benzilic	22.800	22.914	+0.50	22.819	+0.08
	11.400	11.514	+1 00	11.382	−0.16
	5.700	5.795	+1.66	5 681	−0.33

* Calculated from six determination.
In the case of titration with alkali the phenolphthalein colour fades rapidly at the end-point. The first appearance of the pink colour was noted.

Acids can also be determined by treating them with an excess of iodide and iodate solution followed by the titration of the liberated iodine and this can be used as an alternative, often more accurate to alkalimetry[5]. The iodometric method works well with strong acids but failed when applied to weak acids owing to slow reaction rate so that the reaction was not complete in 24 hr[6]. The reaction mixture could not be heated to speed up the determination on account of volatility of iodine. Recently, the addition of solid iodide and iodate has also been suggested for a direct iodometric determination of some organic acids[7]. Kolthoff[8] suggested addition of a known excess of thiosulphate to acid solution containing iodide and iodate and subsequent back-titration of the surplus thiosulphate. But this procedure involves long reaction periods[9]. Moreover, there is a possibility of the thiosulphate reacting with the acid[10] thus vitiating the stoichiometry of the main reaction.

The proposed method is based on the measurements of the iodate consumed rather than on the titration of the liberated iodine when an acid sample is treated with iodide and iodate. With this changed approach it is possible to heat the reaction mixture when the quantitative reaction can be achieved in 3-5 min with acid samples containing 0.025-0.1 meq of the acid. The procedure thus becomes rapid and being iodometric gives sharp end-point even when 0.01 or 0.005 *N* thiosulphate solution is used for titration. This iodometric method can also be adopted for determining acid content in various natural products which are slightly coloured, thereby rendering the neutralisation indicator unsuitable. In evaluating acid content of substances[11] containing components capable of reacting with alkali, the alkalimetry cannot yield correct results. In such cases also the proposed iodometric method possesses a distinct advantage.

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OBITUARY

Priyadaranjan Ray

(Born : *January 16, 1888* ; Died : *December 11, 1982*)

On Saturday December 11, 1982 morning Professor Priyadaranjan Ray passed away after protracted illness at the age of 95 years. An erudite scholar deeply dedicated to his profession, he imbibed in his life the best of Indian traditions and philosophy combined with scientific reasoning, analytical approach and a missionary zeal. In India, he was a pioneer in the field of researches in coordination chemistry in its various aspects and microchemical methods of analysis. His death has left a void in the field of chemical education and chemical research which would be difficult to fill in the near future. For many of us, whose joys and sorrows he used to share and who received all the inspiration and encouragement even in their futile efforts, his death is a great personal loss.

Priyadaranjan Ray was born on January 16, 1888 in a well-known Zamindar (landlord) family in village Noapara in Chittagong district (now in Bangladesh). This Zamindar family was well-known for their benevolence, righteousness and endeavour in the promotion of education and learning.

Priyadaranjan had his early education in his own village school from where he passed the Higher Primary Examination in the first division in the year 1898. The Headmaster of the school was Rashmohan Sen who was a teacher of repute and a man of profound honesty and integrity who influenced greatly young Priyadaranjan. Having finished his primary education in the village school Priyadaranjan joined the Chittagong Collegiate School in 1899. He passed the Entrance Examination (i.e. Final High School Examination) in 1904 in the first division and secured a merit scholarship. In 1906, he passed the F. A. Examination (Intermediate College Examination) from the Chittagong Government College also securing a merit scholarship and a certificate for originality in Bengali composition, a talent which he further cultivated in his later life which produced many excellent scientific and philosophical writings and essays on various socio-economic problems, both in Bengali as well as in English.

In July, 1906 Priyadaranjan came to Calcutta for higher education and joined the first year B. A. class in Presidency College. Here Priyadaranjan came in contact with renowned teachers and educationists like H. M. Parcival, who was then the Principal of the College, Acharya Jagdish Chandra Bose (Sir J. C. Bose) and Acharya Prafulla Chandra Ray (Sir P. C. Ray), all of whom greatly influenced his future career. In 1908, he passed the B. A. Examination from Presidency College with Honours in Chemistry and Physics. In addition to studying Chemistry and Physics he studied and mastered well the three languages English, Bengali and Sanskrit in his B. A. course. Later, he attained proficiency in German language also. Acharya Prafulla Chandra Ray's inspiration took him to Chemistry for his M. A. Examination and he passed this examination from Presidency College in 1911

in the First Class having stood first in order of merit and secured the Calcutta University Gold Medal and Motilal Mullick Gold Medal.

Having received his M. A. degree, Priyadaranjan started research work in Inorganic Chemistry in the Presidency College in Acharya Prafulla Chandra Ray's laboratory. However, on August 12, 1912, he met with a severe accident in the laboratory and as a result lost his left eye and suffered severe injuries to his right eye and other parts of the body for which he was hospitalized for quite some time. It was just before this accident that he had his first research paper published (Die Einwirkung Von Hydrazin und Hydroxylamin auf Ferricyanide und neuer methoden Zur Bestimmung von Hydrazin und Ferricyaniden", P. Ray and H. K. Sen, *Z. anorg. Chem.*, 1912, **76**, 380).

The after effects of the accident and particularly frail vision in the injured right eye prevented him to carry on any work for nearly two years. In 1914 he joined the City College, Calcutta as a Professor of Chemistry and worked in this capacity upto 1918. At this time Sir Ashutosh Mookherjee, who was then Vice-Chancellor of the University of Calcutta, was looking for competent young teachers and research workers to join the newly established University College of Science, Calcutta, to help and assist Acharya Prafulla Chandra Ray, then Sir Tarak Nath Palit Professor and Head of the Department of Chemistry in the University College, to develop the institute to an advanced centre of scientific teaching and research in the country. Priyadaranjan was one of those who was picked up by Sir Ashutosh for this purpose and in the year 1919 Priyadaranjan joined the University College of Science, Calcutta, as Assistant Palit Professor of Chemistry. Here he devoted himself to teaching and research and he was given the charge of organising and developing the Inorganic Chemistry Division. It was by his devotion and perseverance that he soon succeeded, inspite of many odds, to establish a renowned school of modern Inorganic Chemistry in the University College of Science where he devoted the best part of his research career for nearly four decades till his retirement from this institute in December, 1952.

While working as Assistant Palit Professor of Chemistry in the University College of Science, Professor Ray published several original research papers which earned him an international fame. In the words of his *guru* (late) Acharya Prafulla Chandra Ray (1932). "He is regarded as an acknowledged authority on complexes and valency and also on Micro-chemistry and it is my practice to submit my own papers to his criticism and judgement before they are contributed to the Chemical Societies. My Presidential addresses at the annual meetings of the Indian Chemical Society of 1926 and 1929 are based mainly upon his ideas and suggestions. A more silent and unobstrusive worker is seldom to be met with . ...He has already published a score of papers, any one of which if submitted to any University would win for him a doctorate. He has not, however, as yet been able to make up his mind to do this. Events are of two kinds—the silent and the noisy. Priyadaranjan's work comes under the former category".

Priyadaranjan has been a silent worker throughout his life who had no lust for glamour such as foreign travel even in his younger days. It was by much effort that his *guru* Acharya Prafulla Chandra could persuade him to go to Europe on a Ghose Travelling Fellowship of the University of Calcutta as a Visiting Professor to work in the laboratories of the renowned Inorganic Chemist, Professor Fritz Ephraim, in Berne in Switzerland and of the famous Micro-Chemist, Professor Frederic Emich, in Graz in Austria. During his stay abroad, he also visited a number of other research centres in different parts of Europe before returning to India towards the end of 1930.

Priyadaranjan was elected the President of the Chemistry Section of the Indian Science Congress, 1932 In those days this was a unique recognition that could be achieved only by a distinguished chemist by virtue of his scientific contributions and by no other means. In the Bangalore Session of the Indian Science Congress in 1932 he delivered at the Chemistry Section his presidential address on "Doctrine of Valency and the Structure of Chemical Compounds" which was an authoritative account of the then prevailing views on valency and complex compounds, a field in which he had made significant contributions from studies on the magnetic properties of various compounds. In fact, Professor Ray is one of the earliest workers on the systematic application of magnetic properties in the elucidation of the structures of compounds including metal complexes and in determining the valency of a transition metal in its compounds. Professor Wilhelm Klemm (1950), Director, Anorganische-Chemisches Institut, University of Munster, West Germany, who is an acknowledged authority on magnetochemistry mentioned of Professor Ray's contributions as follows : "In giving an account of the modern developments in the field of Inorganic Chemistry I cannot conclude without referring to the contributions of the Indian workers in this field. Mention of names like Raman, Krishnan and P. Ray will in my opinion, suffice for the purpose". In 1932, he was elected an Editorial Collaborator for publication of a comprehensive and authoritative treatise on Analytical Chemistry named "Chemische Analyse" with Professor Wilhelm Botger of Leipzig as the Editor-in-chief. This was in recognition of his significant contributions in developing new analytical methods for detection and estimation, applicable in macro and micro scales, based on the use of new reagents including complexing ligands such as rubeanic acid (1926) which form characteristic complexes with metal ions and is infact the most sensitive reagent for the detection of copper(II) ion known till today. Analytical applications of bismuthiol, quinal-

dinic acid, biguanides, etc. were developed by him later, as well as new colorimetric methods using various organic reagents. In due recognition of his contributions in microchemical and colorimetric methods, Professor Ray was elected (1951) one of the seven members of the Commission of New Reactions of the International Union of Pure and Applied Chemistry to prepare a comprehensive and critical report on the colorimetric methods of analysis which has been documented. He worked in this Commission for 8 years and when he was invited to be a member again he declined suggesting the appointment of a younger member. This is significant.

In 1935, Professor Ray was elected a Foundation Fellow of the then newly established National Institute of Sciences of India (now named Indian National Science Academy). In the year 1937, he was appointed the Khaira Professor of Chemistry, University of Calcutta and became Sir Tarak Nath Palit Professor and Head of the Department of Chemistry, University of Calcutta in 1946 from which post he retired in December, 1952. He had received invitations to attend various International Scientific Conferences in USA, UK, Germany, Sweden, etc. which he declined mainly because of his lack of interest in publicity.

For over 20 years since 1937 Professor Ray published a series of research papers on his studies on the nature of the complexes of different transition metal ions with biguanide and its derivatives. One such ligand has also been used to form a compound of Ag(III) which is the most stable compound of Ag(III) known so far. The results of these authoritative studies have been documented in an invited review article published in the Chemical Reviews in 1960. Professor M. T. Beck (Hungary) commented on it as follows (1961): "I am extremely interested in your work on the chemistry of biguanide complexes. So I was excited to read your impressive review which appears to me a real Gold-mine."

After his retirement from the University of Calcutta he joined the newly established department of Inorganic Chemistry of the Indian Association for the Cultivation of Science, Calcutta, the oldest research institution in India (founded by Dr. Mahendra Lal Sircar in 1886), as the Honorary Professor of Inorganic Chemistry. During his service in the University of Calcutta he was for several years the Hony. Secretary of this institution and was much responsible for its development into an institution of national importance. He was also the Hony. Director of this Institute (1956-58).

During his term as Director he donated a sum of Rs. 30,000/- out of his remuneration to the M. N. Saha Memorial Fund of the Association for the advancement of science and for perpetuating the memory of (late) Professor M. N. Saha. Since he left the Association in 1958 he ceased to be actively associated with any research laboratory. But after his retirement from the Association he actively engaged himself as a Supervisor in charge of History of Science unit of the Indian National Science Academy and guided for several years valuable investigations by a team of workers on the progress of science in ancient India. The compilations on "*Charak-Sanghita*" and "*Susrut-Sanghita*" under his editorship are a few of the outcomes of such activities.

His interests in the History of Science are well-known and he edited "The History of Chemistry in Ancient and Medieval India" (Indian Chemical Society, 1956) which is a completely revised and enlarged version of the book "History of Hindu Chemistry" written by Acharya Prafulla Chandra Ray. He also edited "Fifty Years of Sciences in India—Chemistry" (Indian Science Congress Association, 1964).

Professor Ray is the author of several coveted endowment and memorial lectures of various scientific and national organisations in India.

Porfessor Ray served as the President of a national symposium on the "Chemistry of Coordination Compounds" held at Agra in 1959 under the auspices of the National Academy of Sciences. He was elected the President of the Indian Science News Association for the term 1958-59 and served for several years in the Editorial Board of the journal "Science and Culture".

He was elected the President of the Indian Chemical Society for the term 1947-48 and was an ex-officio Vice-President of the Society in his capacity as a past President during his lifetime. He had also served the Society and its Council in other capacities including Hony. Secretary (1933-36), Hony. Editor (1938-42) and Vice-President (1945-46). He was the President of the 20th International Conference on Coordination Chemistry held in India (1979).

He published nearly 200 original research papers in well-known journals and wrote innumerable articles, both in English and in Bengali, on various topics such as Science, Society, Religion, etc. He was one of those few of his time who was actively associated in the popularization of science through writings in Bengali language.

The Universities of Jadavpur, Burdwan and Calcutta honoured him by awarding the degree of Doctor of Science (*Honoris Causa*).

Apart from his personal scientific contributions Professor Ray also trained up for several decades a band of Inorganic Chemists who have occupied responsible and coveted positions in different educational, scientific and industrial organisations in the country. This creation of a school is no less significant than his own contributions in active research and he may aptly be called the doyen of Inorganic Chemistry in India and about him Professor John C. Bailar, Jr. (USA), a celebrated Inorganic Chemist, expressed (1961) as follows: "He has reasons to be proud of what he has done for the country".

Like his *guru* Acharya Prafulla Chandra Ray, Prof. Priyadaranjan Ray was also a bachelor. In the words of (late) Prof. Pulin Behari Sarkar, "He (Priyadaranjan) imbibed all the great qualities of his *guru* Acharya Ray, like him was a confirmed bachelor with a dedicated life, equally a linguist and nay even a better finished Chemist. He had an unflinching devotion to his *guru* and so worthily got his benedictions . He got by his steady persevering work, recognition not only in India but also abroad".

A man of few words, Professor Ray was always somewhat reserved but very compassionate and honest in his assessments. He was greatly distressed about the present deterioration in research spirit and ethics in the country and had ventilated his views on several occasions in recent times. What pained him most was that while facilities and investments for research are increasing, the output has not been upto expectations. He considered devotion and dedication as the prior needs for any advancement of Science and Technology, since progress depends on men and not on materials and machinery which are merely the tools.

D. Banerjea

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Training and Research in Analytical Chemistry : An Interdisciplinary Science

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A brief survey of the work being pursued in India in the discipline of analytical chemistry has been presented The need of developing novel directions of approach and the use of more sophisticated techniques has been highlighted. Research work in the field of analytical chemistry should be accompanied by a clear understanding of the tools, the limits of precision involved and the basic chemical principles of the process. There should be an active coordination between teaching and research.

IT is a matter of great pleasure for me to contribute this article to the special issue of the Journal of the Indian Chemical Society, being brought out on the occasion of the sixtieth birthday of my friend Professor Arun K. Dey. Prof. Dey's outstanding contributions in the field of Inorganic and Analytical Chemistry, ranging over approximately four decades, are too well known to be enumerated here. Beginning with novel methods[1] of calculation of formation constants of complex ions, Prof. Dey has made significant contributions in the fields of coordination chemistry of lanthanides[2] and inorganic polymers[3] ; the applications of inorganic concepts to analytical chemistry has been his abiding interest and has resulted in internationally recognised contributions from his research school in the fields of chromatography[4], ion exchange[5], electrophoresis[6], ring oven technique[7], ion selective electrodes[8] and spectrophotometric determination of metal ions[9]. In view of his keen interest in teaching and research in analytical chemistry, it appears appropriate to present in this article a brief account of the development of this interdisciplinary field of science.

Analytical chemistry may be defined as the science of *chemical characterization and measurement* With the merging boundaries of conventionally accepted disciplines of science, the meaning of the term *chemical characterization* has been changing and now covers many techniques which would have at one time been considered to belong to the domain of physical analysis or biological assay. Simultaneously, the instruments with which *measurements* are made have been constantly undergoing development. Efforts at improvements in the techniques of characterization and measurements to incorporate more and more complex situations (e.g., ultramicro quantities in large interfering preponderances) constitute major thrusts of research in analytical chemistry. However, fundamental progress in these demanding sophisticated techniques does require a very clear understanding of the theoretical principles involved. In addition, the analytical chemist in his efforts to enlarge the utility of the applications of his science for different disciplines (e.g., meteorology, geology and biology) has to develop a better appreciation of the specific needs of these users and make the analytical procedures as foolproof as possible for those who are not highly trained in analytical chemistry

Conversely, many types of scientists (including chemists of different specialisations) and engineers have been continuously making valuable contributions to analytical chemistry. A physical chemist, for example, may spend some time and effort in improving the time-, spatial- or frequency-resolution of his spectroscopic measurements to draw more reliable and penetrating conclusions in his current area of research. What distinguishes an analytical chemist is that he makes improvements in characterization and measurements his goal rather than means to an end.

Growth of analytical chemistry and India's contribution to the field: In his thought provoking special award address at the Society for Analytical Chemists at Pittsburgh in 1980, H. A. Laitinen[10] presented a graphic account of the phenomenal growth and importance of 'Analytical Chemistry in a Changing World', which makes it clear that analytical chemistry continues to occupy a central place in the overall growth of chemistry. This is depicted by the data in Table 1[11] representing the percentage of chemical publications which were devoted to analytical chemistry.

TABLE 1—RELATIONSHIP BETWEEN CHEMICAL AND ANALYTICAL CHEMICAL LITERATURE FOR 1970

Country	Analytical literature. % of total chemistry	Relative growth rate. T_d Anal / T_d Chem.
U S S. R.	11.2	1.2
U S A.	5.1	0.9
Japan	9 8	0.8
Germany-East & West	6.7	1.2
U K.	10 3	1.1
France	7.1	1.5
The Netherlands	7 4	1.2
Italy	5.9	0.9
World's literature	8.2	1 0

In the above table, the data in the third column again show that the rate of growth of the analytical

chemistry literature is generally higher than the rate of growth of chemical literature as a whole. The comparatively faster growth of literature in analytical chemistry is again depicted by the concept of 'doubling periods' in Table 2[12].

TABLE 2—DOUBLING TIME (d_s) OF SCIENTIFIC LITERATURE

Discipline	d_s
[a]Analytical chemistry	13.9
[a]Chemistry	14 5
[b]Biology	16
[b]Physics	19
[b]Electrical engineering	20
[b]Psychology	25
[b]Economics	13

India's contribution in the realm of analytical chemistry has always been quite substantial, although a number of recent reports dealing with the growth of different branches of chemistry in this country have tended to ignore this. Starting with the highly significant contribution[13] to the list of organic reagents by demonstrating the use of dithio-oxamide (rubeanic acid) in 1926 by P. Ray for the detection of copper, cobalt and nickel, the research work in analytical chemistry has continuously progressed in this country and this has been summarised in two reviews[14,15] upto 1972.

Brooks and Smythe[16] recently reviewed the world progress of analytical chemistry in the period 1910-70. Building upon the previous accounts by Fischer[17] in 1965, these workers compared entries in *Analytical Abstracts* and *Chemical Abstracts* and were able to calculate the percentage of total activity of chemical research in different countries devoted to analytical chemistry (cf., Table 3).

TABLE 3—PERCENTAGE OF ANALYTICAL WORK CARRIED OUT IN VARIOUS COUNTRIES

Country	Year	
	1965	1970
U. S S R.	25.4	28.4
U. S. A	15.8	17.7
Japan	11.0	7.7
Germany	6 4	6.1
U. K.	4.3	5.9
Czechoslovakia	5.3	5.6
France	3.5	2.6
India	3.5	2 6
Scandinavia	0.7	2.1
Romania	3.5	2 0
Poland	4 1	1.8
Spain	1.8	1.5
Netherlands	0 8	1.3
Italy	1.7	1 0
China	3 1	–
Rest of the world	9 1	11.1

In another analysis of *Analytical Abstracts* published in 1977, Braun and coworkers[11] concluded that there were 8311 papers distributed in 741 journals, although there was heavy concentration of 50% and 90% of the papers in only 3% and 36% of the journals respectively. Data for first 50 of the journals are given in Table 4. Two Indian journals, 'The Indian Journal of Chemistry' and the 'Current Science (India)' are included in this list. These workers further extended their analysis to a 'quality' indicator 'impact factor', which has been defined as the ratio of the number of citations made in any year (say 1978) to the material published in the previous two years (say 1976 and 1977) in a particular journal and the total number of articles published

TABLE 4—THE FIRST 50 LEADING JOURNALS ON ANALYTICAL CHEMISTRY COMPUTED FROM ANALYTICAL ABSTRACTS 1977, RANKED BY PRODUCTIVITY

Rank	Journal	No. of papers found	Rank	Journal	No. of papers found
1	J. Chromatogr.	710	26	Rev. Sci. Instr.	52
2	Anal. Chem.	511	27	Lab. Pract	51
3	Anal. Chim. Acta	338	28	J Clin. Chem. Clin Biochem.	51
4	Zh Anal. Khim.	315	29	Pharmazia	46
5	Anal. Biochem.	300	30	Appl. Spectrosc.	45
6	Fresenius Z. Anal. Chem.	212	31	Quim. Anal	40
7	J Assoc Off Anal. Chem.	206	32	Ukr. Khim. Zh.	37
8	Talanta	198	33	Environ. Sci. Technol.	37
9	Bunseki Kagaku	171	34	J. Electroanal. Chem. Interfacial Electrochem.	35
	Zavod Lab.	170			
10	Chem. Anal. (Warsaw)	169	35	Biochem. Med.	34
11	Clin. Chem	161	36	Appl. Opt.	34
12	J Radioanal. Chem.	147	37	J. Amer. Oil. Chem. Soc.	33
13	Analyst	146	38	Bull. Environ. Contam. Toxicol.	33
14	J. Pharm Sci.	132	39	Int. J. Appl. Radiat. Isot.	32
15	Mikrochim. Acta	116	40	*Z Lebensm. -Unters	31
16	Clin. Chim. Acta	109	41	X-Ray Spectrom.	31
17	Anal Lett.	92	42	At. Absorpt. Newsl.	30
18	Chromatographia	91	43	J. Phys. Sci. Instrum.	29
19	Radiochem. Radioanal. Lett.	85	44	Nucl. Instrum. Methods	29
20	J Chromatogr. Sci	76	45	An. Quim.	29
21	Revista Chim. (Bucharest)	75	46	Yukugaku Zasshi	28
22	J. Agric. Food. Chem.	71	47	Curr. Sci. (India)	28
23	Indian J. Chem. Sect. A	60	48	Acta Pol. Pharm.	28
24	Farmatsiya (Moscow)	52	49	Z. Chem. (Leipzig)	27
25			50	Chem. Pharm. Bull. (Tokyo)	27

TABLE 5—IMPACT FACTOR OF LEADING JOURNALS ON ANALYTICAL CHEMISTRY (1978)

Rank	Journal	Impact factor	Rank	Journal	Impact factor
1	Clin. Chem.	3.106	21	X-Ray Spectrom	1.118
2	Anal. Chem.	3.058	22	Chem. Pharm. Bull	0.979
3	J. Chromatogr. Sci.	2.586	23	Fresenius Z. Anal. Chem.	0.930
4	Anal. Biochem.	2.309	24	J. Assoc. Off. Anal. Chem.	0.916
5	J. Chromatogr.	2.302	25	Int. J. Appl. Radiat. Isot.	0.790
6	Appl. Spectrosc.	2.161	26	J. Phys. Sci. Instrum.	0 714
7	Chromatographia	1.972	27	Mikrochim. Acta	0.697
8	Appl. Opt.	1 934	28	J. Radioanal. Chem.	0 685
9	Clin. Chim. Acta	1.676	29	Radiochem. Radioanal Lett.	0.639
10	Analyst	1 666	30	Z. Chem. (Leipzig)	0.623
11	J. Electroanal. Chem. Interfacial Electrochem.	1 525	31	Pharmazie	0.483
			32	Z. Lebensm. Unters. Forsch.	0.455
12	J. Agric. Food Chem.	1.503	33	Bunsek Kagaku	0.410
13	Environ. Sci. Technol.	1.436	34	Zh. Anal. Khim.	0.403
14	Anal. Chim Acta	1.404	35	An Quim.	0.393
15	Anal. Lett.	1 244	36	Indian J. Chem. Sec. A	0 322
16	Talanta	1.182	37	J. Amer. Oil. Chem. Soc.	0.278
17	J. Pharm. Sci.	1.171	38	Acta Pol. Pharm.	0.262
18	J. Clin. Chem. Clin. Biochem.	1 163	39	Curr. Sci. (India)	0.221
19	Nucl. Instrum. Methods	1 141	40	Ukr. Khim. Zh	0.145
20	Rev. Sci. Instr.	1.131	41	Yukugaku Zasshi	0 145
			42	Zavod. Lab.	0.117
			43	Revista Chim. (Bucharest)	0.082

in the same journal during the same two years. The actual data of 1978 impact factors for the top 43 journals are given in Table 5, in which both the Indian journals re erred to in Table 4, do find a place *albeit* very low, alm st at the bottom.

Teaching and research in analytical chemistry: Following the more advanced countries, the typical chemistry curriculum adopted by different universities in this country included qualitative group analysis, titrimetric procedures and gravimetric analysis of mixtures including complex materials such as cement, ores and alloys. In addition, courses in analytical aspects of organic analysis were also included at the higher levels. With the changing techniques actually used in analytical operations in academic and industrial laboratories, the curricula have undergone fast changes in developed countries by the introduction of more specialised courses, for example, in electrochemical and spectrochemical analysis, electronics as well as advanced methods of data acquisition and processing.

In view of the above trends, the observation of Herman Liebhafsky in his 1962 Fischer award address, "Like it or not, the chemistry is going out of analytical chemistry", appears to be quite relevant. While one may not agree with this sweeping statement, yet the pressure on the curriculum and available training time tends to make the learners less and less interested in the fundamental aspects of analytical chemistry, the understanding of which remains as essential as ever for practitioners as well as researchers in analytical chemistry.

In the history of analytical chemistry itself, recognition of the fact that analytical chemistry is not solely empirical in nature was only slowly realised. For example, it is only after many decades of 'empirical recommendations' on the temperature at which a precipitate should be heated in a gravimetric procedure that the matter was investigated by Duval and others in a systematic manner leading to a new branch of study called 'Thermogravimetric Analysis'. The eloquent statement "theory guides, experiment decides" made by the grand analytical chemist of the century, Prof. I. M. Kolthoff is thus continuing to reveal its realism in an ever enhanced manner and hence the task of the teacher in analytical chemistry is becoming all the while more difficult and challenging.

A happy balance between theory and practice in the teaching of analytical chemistry has always been an intricate problem for the framers of curricula and continues to be increasingly so even in the more developed situations. For Universities like ours, the problem becomes even more complex. In the absence of actual sophisticated facilities the extent to which the theoretical features of the same should be taught to enable the learner to use them as these become available to him in later life remains a dilemma for the conscientious teacher, as too much emphasis on theoretical aspects without experimental follow up might give a wrong impression to the learner about the true spirit of this experimental science. Obviously, the resolution of the above dilemma would depend upon the facilities (physical as well as technical) available in any situation, but the following aspects (many of which represent points of special weakness in our system) deserve our special consideration :

(i) training in instrumentation and fabrication of simple analytical equipments involving glass blowing or knowledge of basic electronics, i.e., inculcation of what is sometimes termed as 'instrumentation culture';

(ii) a statistical analysis of the experimental data drawing out clearly the 'limits of error' involved in different steps and representing clearly the actual 'precision limits' of the final results. (The extent to which these

steps receive attention in modern analytical chemistry is illustrated by defining clearly the 'guidelines for data acquisition and data quality evaluation' in environment chemistry[18];

(iii) a comparative study of the accuracy of the results obtained by various (classical as well as modern) methods of analysis (the quality of contributions from our laboratories could have been enhanced considerably if this aspect was emphasized in studying the possible interferences as well as in representing the final results in significant figures);

(iv) planning the exercises and problems at the teaching as well as research levels around real life situations rather than basing them only on artificial makeups (a close liaison and cooperation between university laboratories and industrial and other organisations requiring new analytical procedures could be of immense mutual benefit in this direction),

(v) adequate theoretical background and clearer understanding of the basic principles involved in any analytical procedures;

(vi) coordination between teaching and research should be encouraged by open ended exercises particularly at the post-graduate level and by formulating problems at the research level from the experiences gained and difficulties faced in such exercises in the teaching laboratories.

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Teaching Microchemistry in Industry Versus Teaching in a University

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In an industrial company, the beginner must be able to produce results in as short a time as possible so he or she is taught one determination at a time, whereas in a university, the student receives a full course.

TWO methods of teaching microchemistry are in general use. Industrial companies are interested in having the new employee to be able to produce results in as short a time as possible and concentrate on having he or she becoming efficient in one determination. Some companies employ persons having college or university degrees while others use persons who have no degree but who have had elementary courses in chemistry. In the author's laboratory at Hoffmann-La Roche, before he retired, he had all college or university graduates who have had courses in analytical chemistry (macro), organic chemistry and in some cases physical chemistry.

After being taught the use of the microchemical balance, the individual was allowed to determine metals by the ashing technique, which he continued to do for several days to gain more weighing experience.

The next step was the teaching of the determination of nitrogen by the Dumas method. After repeating this a number of times during the next few weeks, the beginner was experienced enough to be allowed to "graduate" from running known test compounds to do so on research samples, and was then kept doing this determination for several months

Next followed, using the same procedure, the determinations of carbon-hydrogen by the classical method, halogens, sulfur, phosphorus, nitrogen by the Kjeldahl method, arsenic, automatic carbon-hydrogen-nitrogen, alkoxyl, molecular weight, etc., all of the determinations described in the author's text book[1]. Obviously, the more experienced the individual became, the less time and number of test compounds were needed when a new determination was done. Depending upon the person, one to two years was required before analysts were efficient in all types of determinations. In this way there could be rotation of the work, which was necessary to prevent monotony.

At the University, the author gives a one semester course in which the students spend six hours per week for fourteen weeks in the laboratory. Although there have been as many as twenty-six students taking the course at one time, the course is operated on a "by arrangement" schedule basis so that not more than four students are in the laboratory at any one time. This allows for much individual attention so that the students receive the extra benefit. The object of the course is to teach students how to handle small amounts of material with accuracy and precision, rather than to create microchemists The students must have passed courses in analytical chemistry (macro) and organic chemistry. A few of the students are third year undergraduates and a few are graduate students who are candidates for the master or doctor degree. The majority are in their last semester before receiving the bachelor degree

Each student is required to determine (in duplicate) halogens by the Carius method[1] and the oxygen flask mercurimetric method[2], nitrogen by both the Dumas[1] and Kjeldahl[1] methods, carbon-hydrogen by the classical method[1], carbon-hydrogen-nitrogen by automatically, arsenic[1], sulfur[1], phosphorus gravimetrically[1] and titrimetrically[3], alkoxyl[1], molecular weight by the two isothermal distillation methods[1], boiling points, melting points[1] and specific gravity[1]. The results obtained are unusually good. Some students obtain acceptable results[1] in as many as twenty-five out of twenty-six or twenty-seven determinations.

After having taken the regular course, some students do research, as for example the work done on the alkoxyl determination[4], in which it was found that by using the regular apparatus and procedure[1], the sample size could be reduced to as low as less than 100 μg and acceptable results[1] obtained consistently.

After teaching the course for the past thirteen years, during which approximately two hundred students took the course only four have positions as microchemists Many of the others repeatedly advise that, although they are not doing actual micro work, their micro training has been of extreme value to them in their fields.

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Some Interesting Aspects of the Chemistry of Platinum

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PLATINUM is one of the least reactive of metals. It does not tarnish and is insoluble in even the strongest of acids. Simple (hydrated) platinous and platinic ions are almost unknown. In spite of these limitations, the chemistry of platinum is extremely varied and interesting and offers a fertile field for investigation. The common oxidation states of platinum are +2 and +4, but compounds are known in which several other oxidation states are shown. Interesting examples are $[Pt(P\phi_3)_3]$ and $[Pt(P\phi_3)_4]$, in which the metal is formally in the zero oxidation state, and in the first of which the metal has the unusual coordination member of three[1]. Even fractional oxidation states exist in such compounds as $Cs_{1.75}[Pt(CN)_4].2H_2O$, $Rb_{1.6}[Pt(CN)_4].2H_2O$, $[C(NH_2)_3]_2[Pt(CN)_4]Br_{0.25}.H_2O$ and $K_{1.64}[Pt(C_2O_4)_2)]$[2]. These are important because of their electronic properties. In compounds such as $Pt_3Sn_8Cl_{20}$[3], it is futile to try to assign an oxidation state.

In this paper, we are concerned chiefly with the coordination compounds of platinum in the +2 and +4 oxidation states. In the former, platinum usually shows a coordination number of four, but in the trigonal bipyramidal ion $[Pt(SnCl_3)_5]^{3-}$, the coordination number is five[4]. Many of the compounds in which the coordination number is four have high catalytic power, especially for hydrogenation. In these complexes, there is one empty p orbital, through which a carbon-carbon double bond can attach itself to the metal.

	5d					6s	6p		
$Pt^{(II)}$	0	0	0	0	—	—	--	—	—
$[PtX_4]^{2-}$	0	0	0	0	X	X	X	X	—

We have used this catalytic property in the selective hydrogenation of soybean oil, which is a mixture of glycerides of several long chain carboxylic acids, with all of the double bonds in the *cis* configuration:

Most of the soybean oil of commerce goes into food products such as oleomargarine and salad oils. The triply unsaturated linolenic ester, which is present in the oil to the extent of 7-10%, has an unpleasant taste, and many efforts have been made to hydrogenate one double bond in this ester without affecting the other double bonds in the molecule and without hydrogenating the linoleic or oleic esters. Complete saturation must be avoided at all costs, as the saturated esters are hard to digest.

In order to avoid the complication of having three acid chains (perhaps all different) in one molecule, it has been customary in research studies to replace the glyceride unit with methyl groups. My colleagues and I have made extensive studies of the selective hydrogenation of soybean oil, using as the hydrogenation catalyst, a mixture of *bis*-diphenylphosphine-dichloro platinum(II) and several equivalents of tin(II) chloride, thus generating the complex $[Pt(P\phi_3)_2(SnCl_3)Cl]$, which, upon hydrogenation, evidently becomes $[Pt(P\phi_3)_2(SnCl_3)H]$[5]. With this catalyst, it is easily possible to hydrogenate *all but one* double bond. When the catalyst is immobilized by attaching it to polystyrene, it is possible to hydrogenate one double bond of linolenic ester, leaving two, mostly, however, in the *trans*-form. The details of this work have been described recently and need not be repeated[6]. The subject is mentioned here only to call attention to the catalytic power of platinum(II) complexes.

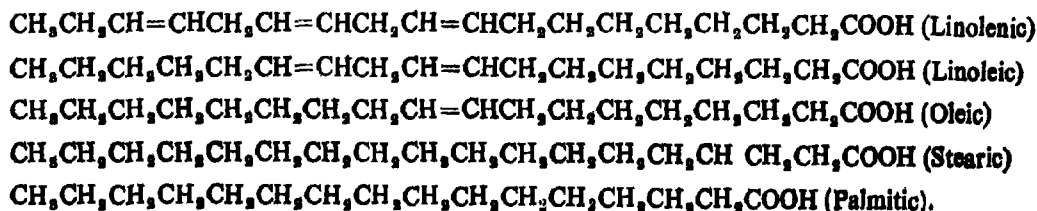
Another important application of platinum complexes is in the treatment of cancer. In 1965, Barnett Rosenberg at Michigan State University observed that *cis*-dichlorodiammine platinum has the ability to inhibit the division of *Escherichia coli* into separated cells, though it does not inhibit the growth of the cells[7]. This led him to the suggestion that this compound might be effective in the treatment of cancer and, indeed, experiment showed this to be correct. The compound is now being used clinically, under the name cisplatin, in the treatment of certain cancers. Needless to say, Rosenberg's exciting discovery has stimulated a great deal of work in this field, and something over

$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$ (Linolenic)

$CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$ (Linoleic)

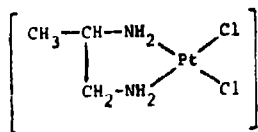
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$ (Oleic)

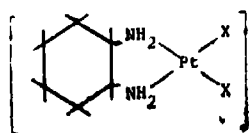
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH\ CH_2CH_2COOH$ (Stearic)

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$ (Palmitic).

twelve hundred compounds have now been synthesized and tested. Most of these contain platinum, but other metals of the platinum family have been tried too. Cisplatin is not an ideal drug, for it is not as effective as we might wish, it is only very slightly soluble and it is horribly toxic. From the many experiments that have been carried out, certain "rules" have been derived. First, the compound must contain two groups which are tightly bound to the platinum and two which are *slowly* hydrolyzed off. The tightly bound groups may be ammonia molecules, as in cisplatin, or they may be amine molecules of a wide variety. Evidently there must be at least one hydrogen atom on the ammine nitrogen. Second, the hydrolyzable groups must be displaced slowly. Nitrato groups will not do, for they are hydrolyzed off too rapidly ; cyano groups are ineffective because they are not hydrolyzed off at all. Chloro groups are satisfactory, their hydrolysis in the body being somewhat inhibited by the presence of chloride ion in body fluids. Other groups that have been found to be effective include sulphato, gluconurato and pyromellito. Supposedly, the non-ionic cisplatin dissolves to a slight extent in the fatty tissue of the body. It is held there until reaction with water converts it to the ionic aqua complex *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ or the hydroxo-aqua complex *cis*-$[Pt(NH_3)_2(H_2O)OH]^+$. These then attach themselves to the strands of the diseased DNA, the nitrogen atoms of the nucleic acid displacing the aqua and/or hydroxo groups. Compounds in which the hydrolyzable groups are *trans* to each other are completely ineffective.

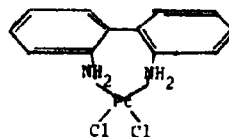
It should be noted in passing that this picture does not tell the whole story, for some compounds that do not resemble cisplatin closely have been found to be effective. Such a one is the dimeric rhodium(II) acetate hydrate, $[Rh_2(CH_3COO)_4(H_2O)_2]^8$.

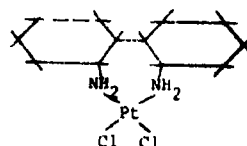
Optical isomers differ not only in the direction in which they rotate the plane of polarized light but also in their reactivity with other chiral substances. This suggests that the enantiomers of platinum compounds might have different effectiveness in the treatment of cancer. Optical activity of a planar platinum complex can be achieved by using an optically active ligand. Rosenberg tried the propylenediamine complex but found little

[Structure: CH_3—CH—NH_2 / CH_2—NH_2 chelated to Pt with two Cl]

difference in the effectiveness of the two isomers[9]. Kidani used 1,2-cyclohexanediamine, of which the *trans* form is chiral[10].

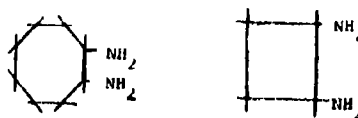
[Structure: cyclohexane-1,2-diamine (NH_2, NH_2) chelated to Pt with two X]

He found the levo-*trans* isomer to be more effective than the dextro-*trans* isomer, which, in turn, is more effective than the optically inactive *cis* isomer.

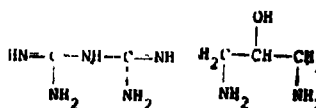
We have applied ourselves to this problem too. The first compounds which we made contained 2,2'-diaminobiphenyl as the ligand.

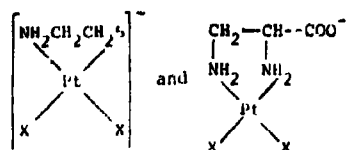
[Structure: 2,2'-diaminobiphenyl (NH_2, NH_2) chelated to Pt with Cl, Cl]

This compound owes its chirality to the fact that the two phenyl rings cannot lie in the same plane but must be tilted with respect to each other, thus assuming a propellor-like configuration. We did not separate the isomers but submitted the racemic material for testing. It has some effect but not enough to warrant further work. In the mean time we learned that aliphatic groups have been found to be better than aromatic ones, so we prepared the cyclohexane analogue.

[Structure: bicyclohexyl-2,2'-diamine (NH_2, NH_2) chelated to Pt with Cl, Cl]

The rings in this compound are not planar as they are in the biphenyl derivative, but they still must be held in "tilted" positions and the platinum compound should be optically active. The resolution of this compound is being studied by Dr. Masahide Noji, who prepared the compound in our laboratory and is now continuing the work in Japan.

Currently, we are working on this problem from two angles—altering the nature of the asymmetric ring and increasing the solubility of the complex. In some cases these objectives overlap. We have prepared 1,2-cyclooctanediamine, which is similar to Kidani's cyclohexanediamine, but because of its larger size, should be more flexible. We have considered going the other way too, to the cyclobutanediamine but have not attempted any syntheses In each case there are symmetrical *cis* and chiral *trans* isomers

[Structures: 1,2-cyclooctanediamine (NH_2, NH_2); 1,2-cyclobutanediamine (NH_2, NH_2)]

For increase in solubility, we are introducing functional groups, as with the ligands biguanide and 2-hydroxy-1,3-diaminopropane or by making the

[Structures: HN=C(NH_2)—NH—C(NH_2)=NH; H_2C(NH_2)—CH(OH)—CH_2(NH_2)]

complex ionic by using a bidentate, negative ion as the ligand.

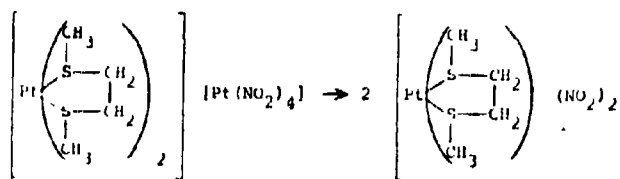
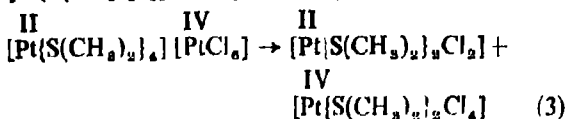
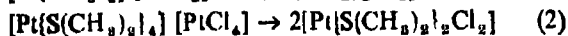
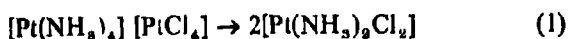
$$\left[\begin{matrix} NH_2CH_2CH_2S \\ Pt \\ X \quad X \end{matrix} \right]^- \quad \text{and} \quad \begin{matrix} CH_2—CH\text{--}COO^- \\ NH_2 \quad NH_2 \\ Pt \\ X \quad X \end{matrix}$$

The 2,3-diaminopropionic acid complex resembles the ethylenediamine complex, which has been shown to be effective against certain cancers but is insoluble. The presence of the carboxyl group gives good solubility but whether the chirality of the carbon atom will give the two isomers different physiological properties remains to be seen.

Quite a different kind of platinum chemistry is also underway in our laboratory. The famous Russian chemist Chugaev observed that some complexes containing platinum in both the cation and anion undergo an interesting disproportionation reaction when they are heated. Some examples are

$$[Pt(NH_3)_4]\,[PtCl_4] \rightarrow 2[Pt(NH_3)_2Cl_2] \quad (1)$$

$$[Pt\{S(CH_3)_2\}_4]\,[PtCl_4] \rightarrow 2[Pt\{S(CH_3)_2\}_2Cl_2] \quad (2)$$

$$\overset{II}{[Pt\{S(CH_3)_2\}_4]}\,\overset{IV}{[PtCl_6]} \rightarrow \overset{II}{[Pt\{S(CH_3)_2\}_2Cl_2]} + \overset{IV}{[Pt\{S(CH_3)_2\}_2Cl_4]} \quad (3)$$

$$\left[Pt\left(\begin{matrix} CH_3 \\ S—CH_2 \\ S—CH_2 \\ CH_3 \end{matrix} \right)_2 \right] [Pt(NO_2)_4] \rightarrow 2 \left[Pt\left(\begin{matrix} CH_3 \\ S—CH_2 \\ S—CH_2 \\ CH_3 \end{matrix} \right) (NO_2)_2 \right]$$

Chugaev had no way to study the mechanism of these reactions, and we are interested in pursuing this part of the problem. All of the ions concerned, except those in the third example, are planar and are probably stacked, with cations and anions alternating (This has, however, not yet been proven experimentally in all cases). If that is the case, we can imagine that there are residual forces between the ligands in each plane and the platinum atoms in the adjoining planes (Fig. 1).

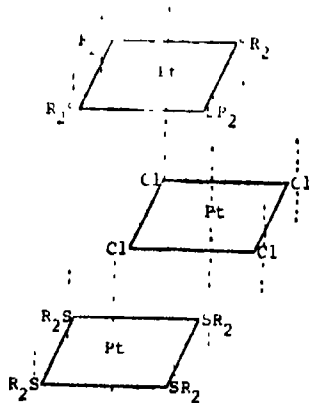



Fig. 1

Upon heating, these residual forces may bring about the rearrangement. With the ammonia complex $[Pt(NH_3)_4]$ $[PtCl_4]$, these forces would be weak and in accordance with this, the disproportionation reaction in that case takes place at a much higher temperature than in the other cases.

For the fourth example above, we must have a slightly different picture, for the entire molecule of dithioether migrates from one platinum atom to the next (Fig. 2).

To determine whether the disproportionation takes place in steps Dr. Hideyoshi Morita, working in our laboratory, prepared the ions $[Pt(Me_2S)_3Cl]^+$ and $[Pt(Me_2S)Cl_3]^-$. He expected, when he mixed solutions of these, to obtain the salt $[Pt(Me_2S)_3Cl]$-$[Pt(Me_2S)Cl_3]$. Much to our surprise, he obtained instead the final product of the disproportionation, $[Pt(Me_2S)_2Cl_2]$. If the reaction takes place in steps, the second step must be very rapid. We do not yet know the mechanism of this reaction, but the work is still in progress

No survey of the chemistry of platinum is complete without mention of the many isopolynuclear compounds which it forms. These contain

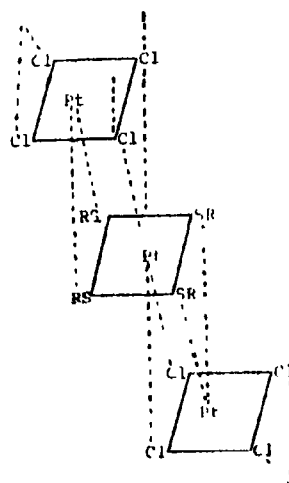



Fig. 2

from two to twenty six atoms of platinum per molecule[15]. The most complex compounds which have yet been prepared are $[Pt_{19}(CO)_{22}]^{4-}$ and $[Pt_{26}(CO)_{32}]^{16}$

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Intramolecular π-π Interactions in Metal "Capped" Porphyrins

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Soret maxima of Zn(C_2-Cap), Zn(C_3-Cap) and Zn(TPP) were recorded in cyclohexane and toluene. In cyclohexane, a progressive red shift in the order, C_3-Cap>C_2-Cap>TPP, is observed. This is attributed to the intramolecular interaction between the porphyrin plane and the aromatic cap of the capped porphyrins. Accordingly, the steric hindrance to O_2 binding inside the cap is perhaps greater in C_3-Cap than in C_2-Cap. This is reflected in the lower oxygen affinity of Fe(C_3-Cap)(1,2-Me_2Im) relative to the C_2 Cap analogue.

METAL complexes of "capped" porphyrins (Fig. 1), which are ortho-substituted tetraphenylporphyrins, have been prepared as model compounds for hemoglobin and myoglobin[1,2]. The two capped porphyrins, C_2-Cap and C_3-Cap[3], differ only by one methylene group in each of the four chains linking the aromatic cap to the porphyrin plane. It had been assumed that the "tight" C_2-Cap would offer a greater steric barrier to the addition of O_2 inside the cap than would C_3-Cap, but oxygenation studies of iron(II) complexes of C_2-Cap and C_3-Cap showed that Fe(C_3-Cap)(1,2-Me_2Im) has a lower O_2 affinity than does Fe(C_2-Cap)(1,2-Me_2-Im)[4,5]. Both capped complexes have a lower O_2 affinity than the Fe(TPP)(1,2-Me_2Im).
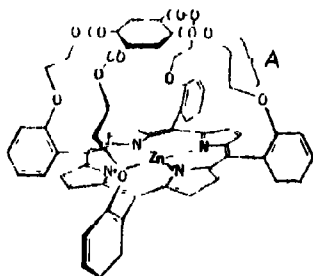
Fig. 1 Zinc(II) "capped" porphyrins.

Porphyrins and metalloporphyrins have been shown to have a tendency to π-complex to π-donors and acceptors and even to aromatic hydrocarbons such as toluene[6-9]. We suggest that the aromatic cap in the capped porphyrins too have the potential to solvate the porphyrin. Our studies indicate that the two aromatic planes in C_3-Cap have greater π-π interaction than does C_2-Cap, suggesting that the aromatic planes are closer together in C_3-Cap, prehaps due to the greater flexibility of the longer straps in this molecule. Evidence in support of this is provided by the observed red shift in the Soret maxima of Zn(II) complexes of C_2-Cap and C_3-Cap relative to Zn(TPP).

Experimental

Zn(TPP), Zn(C_2-Cap) and Zn(C_3-Cap) were prepared following the methods of Baldwin and coworkers[10] from the free bases and characterized by mass spectrometric analysis. Aldrich spectrophotometric grade cyclohexane was stored over Linde 4A molecular sieves. Reagent grade toluene and benzene were distilled under N_2 from sodium benzophenone ketyl.

Spectra of the Zn(Por) complexes in cyclohexane, benzene and toluene were recorded at room temperature on a Cary Model 14 UV-visible spectrophotometer using quartz cells with a 1 cm path length.

Results and Discussion

The Soret maxima of Zn(C_2-Cap) and Zn(C_3-Cap) in aromatic and nonaromatic solvents are presented in Table 1. These may be compared with the corresponding values for the open complex, Zn(TPP), as reference. Due to limited solubility of the complexes in cyclohexane, suitable high concentrations could not be obtained for significant absorbance in the visible region.

TABLE 1—SORET MAXIMA OF ZINC PROPHYRIN COMPLEXES IN DIFFERENT SOLVENTS

Zn(Por)	Position of Soret band (nm) in Cyclohexane	Benzene	Toluene
Zn(TPP)	416	423.5	423 5
Zn(C_2-Cap)	419	423 5	423.5
Zn(C_3-Cap)	424	424	424

In order to look at the π-π interactions between the aromatic top of the cap and the porphyrin plane in absence of axial ligands and solvent interactions, the noncoordinating and nonpolar solvent cyclohexane was used. The spectra show (Table 1) that the Soret band of C_3-Cap has been red shifted by 5 nm with respect to C_2-Cap, and the shift is 8 nm in comparison with TPP. For TPP and C_2-Cap there is a red shift in the aromatic solvents, whereas C_3-Cap does not exhibit any difference between

aromatic and nonaromatic solvents. Soret maxima of metal complexes of porphyrins are sensitive to differences in groups at the periphery of the porphyrin ring, in axial ligands and in solvents[11]. Lewis acid-base interactions of metalloporphyrins with neutral ligands cause a red shift in this spectral characteristic, and the shift increases directly with the magnitude of interaction[12,13]. Taking zinc mesoporphyrin IX dimethyl ester in cyclohexane as the reference (Soret 397 nm), Corwin and coworkers[14] observed a red shift of 5 nm in toluene for this compound. A variety of nonpolar solvents also cause similar red shifts due to adduct formation[15]. Interestingly, π-donors as well as π-acceptors shift the Soret band in the same direction.

Based on these observations and considering the aromatic nature of the cap, it seems reasonable to ascribe the red shifts in these compounds to π-π interaction between the porphyrin and the aromatic top of the cap. The extent of this interaction in C_3-Cap is perhaps equivalent to the interaction between TPP and toluene. Hence in toluene, Zn(TPP) has a maximum which is the same as that for $Zn(C_3$-Cap) in all the solvents.

A comparison of the Soret band positions of C_2-Cap and C_3-Cap with that of TPP shows, at least qualitatively, that the intramolecular π-π interaction is greater in $Zn(C_3$-Cap) than in $Zn(C_2$-Cap). This is in accord with the observation[4,5] that the O_2 affinity of $Fe(C_2$-Cap)(1,2-Me_2Im) is greater than that of the corresponding C_3-Cap complex, and that both have a lower dioxygen affinity than does the open analogue complex, Fe(TPP) (1,2-Me_2Im).

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Chaotropic Ions and Acid Buffers as Eluents in Ligand Purification Using Semiautomated Affinity Chromatography

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A semiautomated technique using the principle of affinity chromatograhy has been developed for large scale purification of biospecific ligands Among chaotropic ions and acid buffers as eluents, NaSCN proved to be a better eluting agent for CEA (carcinoembroynic antigen). The chaotropic ions ($MgCl_2$ and NaSCN), in general, were better eluents than acid buffers. The study was extended using biogel P-60, P-200 and P-300, as immunoadsorbents Binding capacity of the three gels were in the ratio of 1.0 : 2.8 : 2.38. Use of P-300 as immunoadsorbent helped in the recovery of high affinity antibody.

ADVANCES in the field of immunology and immunochemistry[1] during the past two decades have necessitated an increasing need for purified ligands for detection or quantitation of biological substances in body fluids. Insoluble immunoadsorbent, utilizing the principle of affinity chromatography, serves as an elegant purification technique[2,3]. It is based on the formation of an immune complex between ligand and receptor components formed by covalently linking proteins to each other or to insoluble supports such as agar or sephadex gel. After the formation of the complex, the gel is washed free of uncoupled proteins. Thereafter, the complex is dissociated yielding the desired substances in a highly purified state. This principle has been used by various workers[4,5] utilizing techniques like column or batch for ligand purification. Both of these techniques are cumbersome and time-consuming whenever a sizable quantity of purified ligand is needed. This report describes an effort to semiautomate the batch technique and the experience with the apparatus using different types of immunoadsorbents, ligands and ligand-dissociating fluids.

Apparatus :

1. *Amicon Company pressure dialysis units, Models No. 402 and 12 :*

Amicon Model No. 12 was used for processing small amounts of immunoadsorbent (about 1.5-2.0 g), whereas Model No. 402 was used for larger quantities (about 75-100 g). The molecular membranes in the latter units were replaced by nylon polyester cloth (pore size 400×400 which allowed fluids to escape while retaining the immunoadsorbents). Positive pressure (2-5 pounds/in²) from a nitrogen tank was used to rapidly evacuate the fluids from the unit's chambers.

2. *Home made elution unit :*

The chambers of the units are constructed of tubular acrylic plastic measuring 10.5 cm in length and 7.5 cm in outside diameters. The walls measure 0.5 cm in thickness. Both ends are threaded for a
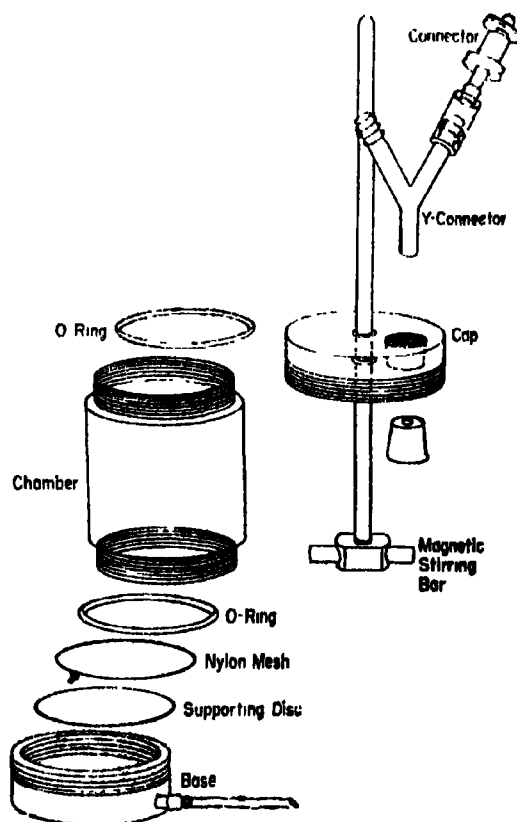
Fig. 1. Exploded view of the elution chamber.

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distance of 1.5 cm. The ends are closed by threaded end pieces (cap and base) measuring 9 cm in diameter and 3 cm in depth, each of which contains an 0-ring measuring 7.5 cm in diameter. The base is fitted with a porous filter support disc which, in turn, is covered with a nylon filter cloth secured in position by an 0-ring. A discharge tube measuring 2×0.5 cm (to drain the chamber) is included in the base as shown in Fig. 1.

A 2.6 cm hole to accommodate a No. 4 rubber stopper is drilled through the cap 2 cm from one edge. A teflon rod measuring 18 cm in length and 1 cm in diameter is suspended from the midportion of the upper cap by two tightly fitted grommets recessed in the inner and outer surfaces of the cap, respectively. A swivel, inserted into the lower end of the teflon rod, in turn, is fitted with a teflon-coated magnetic stirring bar measuring 5.4×1 cm. Although airtight, the teflon rod may be raised or lowered.

The rubber stopper is inserted from the inside of the cap to prevent its displacement under pressure. A plastic Y-tube (size 5/16") contained in the stopper allows the latter to be displaced, but prevents it from falling into the chamber. One end (of the two external openings) in the Y-tube is connected to a two-part plastic connector; the wall of the outer portion of the connector is closed by fusing the edges with a flame. The other end of the Y-tube is connected to a common supply tube (C).
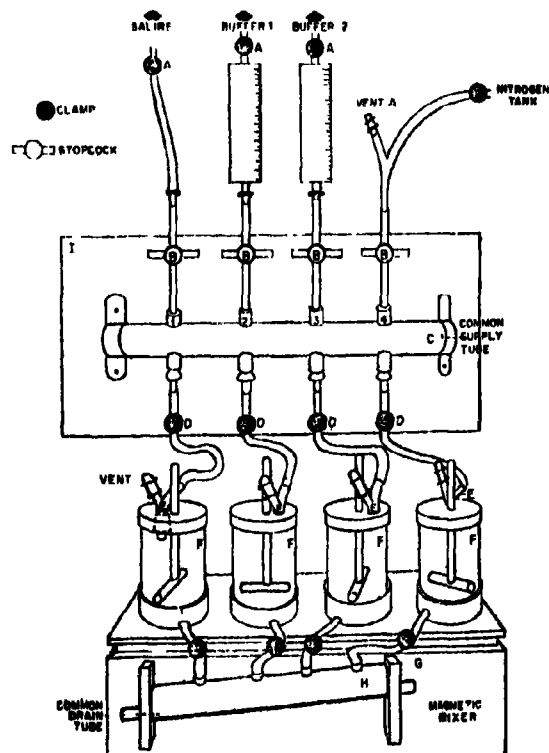
Fig. 2. Semiautomated batch elution from affinity type immunoadsorbent.

Four such elution units are normally positioned on multi-magnetic stirrer platform (Fig. 2); their respective discharge tubes are connected below to a closed, common plastic drainage tube (H) filled with a spout at one end. The tube (3.0×3.5 cm) is held at an angle of 15° to the table top by two feet, unequal in heights, measuring respectively 4 and 2 cm. Each of the elution units is connected above to the common supply tube (C) by plastic tubing (fitted with clamps).

The common supply tube containing four entry portals (labeled 1,2,3 and 4 in Fig. 2) is connected to a supply of saline, buffer No. 1, buffer No. 2 or chaotropic solution and to a nitrogen tank, respectively. Inserted between the buffer supply No. 1 and No. 2 are two disposable 100 ml plastic burettes. Clamps are attached to the tubing leading from the saline, buffers, chaotropic solution and N_2 tank supplies. The apparatus between the salines and the elutions units are attached to a wooden backboard which can be tilted to completely empty the common supply tube when necessary. Operation of this home-made unit is essentially similar to the commercial units.

Materials and reagents :

Immunosorbents : Protein co-polymer, Sephrose and Biogel P-300, each containing a complexed monospecific antibody or antigen.

Phosphate buffer saline (PBS),

Glycine HCl 0.1 *M* pH 2.5,

Chaotropic ionic solution (3 *M* $MgCl_2$ and 3 *M* NaSCN),

Urine containing kappa L-chains obtained from patient with kappa-type myeloma, lypholized and stored at room temperature until the kappa L-chains were purified,

Carcinoembroyonic antigen was purified from a case of colonic carcinoma.

Experimental

Radiolabeled studies (preliminary experiments) : To avoid contamination of the apparatus by radioactive materials, the following preliminary experiments were carried out with radio-labeled materials in test tubes :

1) Capacity studies of different type gels (P-60, P-200, P-300).

2) Elution studies using acid buffer at different pHs.

3) Elution studies using chaotropic ions.

Non radio-labeled studies : Those studies were carried out using the apparatus as described earlier.

a) Purification of kappa L-chains.

Preparation of immunoadsorbents :

Goat anti-human IgG and rabbit anti-CEA antibody (γ-fractions) respectively were covalently

bonded to Biogel P-60 (100-200 mesh), P-200 (100-200 mesh) and P-300 (-400 mesh) as directed by Avrameas and Ternyck[6] by first activating the gels by using 6% solution of glutaraldehyde in 0.1*M* phosphate buffer adjusted to *p*H 7.0. Thirty (30) mg of the antiserum was mixed with 10 ml of centrifuged and activated beads for sensitization.

Simultaneously 10 mg of γ-fractions of anti-IgG antibody and anti-CEA antibody were covalently bonded to 1 g of CNBr-activated Sephrose 4B as directed by Pharmacia[7].

Preparation of antisera :

Antisera were produced in rabbits against kappa L-chains and carcinoembryonic antigen (CEA) as previously described[8]. The antisera were absorbed by insolubilized serum proteins, and in the case of anti-CEA, by insolubilized extracts of normal colon until they were monospecific. Their IgG fractions were then isolated as described eariler[1].

Preparation of radio-labeled antigen :

One hundred (100) mg of chromatographically purified human IgG in 50 ml of 0.2 *M* phosphate buffer *p*H 7.2 was mixed with 10 ml of $Na^{125}I$ (1 mCi) and 25 ml of enzymobead and the reaction was allowed to proceed for 20 min at room temp using 1% *beta* D-glucose as suggested by Biorad[9]. ^{125}I tagged protein was separated from unattached ^{125}I by gel filtration in Sephadex G-50. ^{125}I-CEA was obtained from a commercial source (Hoffman-La Roche, Nutley, N. J. 07110).

Saturation of immunoadsorbents with radiotagged ligands (IgG and CEA) :

Radiolabeled antigens were incubated with their homologous immunoadsorbents monospecific for IgG and CEA, respectively. The incubations were allowed to continue overnight following which the gels were thoroughly washed with PBS. The radiolabeled ligands were then eluted with 0.1*M* acetate buffer *p*H 4.0 and 0.1*M* glycine-HCl buffers *p*H 3.5 to 1.4 and with chaotropic ionic solutions (3*M* $MgCl_2$ and 3*M* NaSCN).

Binding capacity of polyacrylamide gels :

Equal amounts of Biogel P-60, P-200 and P-300 were saturated with an excess of ^{125}I-IgG (11.5 mg). After overnight incubation, the gels were thoroughly washed, the radioactivity counted and the amount of protein associated with each gel was determined. Controls (unsensitized gels) were to react with equal amounts of labeled proteins under identical conditions and the nonspecific attached radioactivity was then to be determined.

Elution procedure :

In the preliminary experiment, equal amounts of complexed immunoadsorbents (Biogel and Sephrose 4B) were taken in different tubes coated with BSA, and mixed with equal volume of various ligand dissociating fluids at room temp. At a regular interval extending from 30 min to 92 hr, the tubes were centrifuged and radioactivity of an aliquot counted following which the beads were resuspended. Results are recorded in Tables 1 and 2.

The purification procedure was further extended using affinity chromatography. According to their binding capacities, amounts of P-60, P-200 and P-300 complexed immunoadsorbents containing equal amount of attached antigen were equilibrated in different columns and washed thoroughly with PBS till the washings were very near the background counts. Antigen (^{125}I-CEA) was eluted with 3*M* NaSCN and the eluates counted.

Use of semi-automated technique was also made to study the purification of a protein on a mass scale. In one set, polymerized normal human serum was complexed with goat anti-human and a homologous purified antiserum was eluted by 3*M* $MgCl_2$. In another set, human kappa light chain was isolated from anti-kappa chain immunoadsorbent and kappa chain lypholized urine using 0.1*M* glycine-HCl *p*H 2.4 as the elution fluid.

Recovery of kappa L-chains :

Lypholized urine containing kappa L-chains (78.6 mg) was incubated with 40 ml of P-300 sensi-

TABLE 1—ELUTION OF IgG (%) USING BATCH TECHNIQUE

Elution system	Time: 30 min		60 min		120 min		180 min		20 hr		44 hr		68 hr	
	P-300	Seph 4B	P-300	Seph 4B	P-300	Seph 4B	P-300	Seph 4B	P-300	Seph 4B	P-300	Seph 4B	P-300	Seph 4B
0.1 *M* acetate *p*H 4.0	-	-	0.5	0.0	0.9	0.0	0.5	0.0	1.2	0.4	3.5	0.2	-	0.6
0.1 *M* Gly-HCl *p*H 3.5	-	-	7.7	10.6	10.5	9.6	12.3	9.7	27.9	13.0	42.9	23.6	-	33.3
0.1 *M* Gly-HCl *p*H 3.0	-	-	15.6	40.2	24.1	28.5	25.2	24.3	35.2	23.7	46.3	24.3	-	20.5
0.1 *M* Gly-HCl *p*H 2.5	-	-	33.8	56.8	41.1	53.6	49.8	53.1	59.2	45.4	64.3	45.4	-	43.8
0.1 *M* Gly-HCl *p*H 2.0	-	-	47.5	57 3	52.6	56.8	53.5	54.1	59.3	53.8	55.8	53.7	-	51.0
0.1 *M* NaCl-HCl *p*H 1.4	-	-	55.2	61.6	54.3	51.0	54.6	48.1	56.0	50.0	59.9	36.9	-	32.7
3 *M* $MgCl_2$	-	66.5	19.2	74.9	25.6	72.0	37.4	76.2	37.7	88.0	52.8	82.4	-	80.0
3 *M* NaSCN	-	70.7	22.0	77 8	29.9	84 0	29.2	85.0	42.3	91.2	51.1	—	-	-

TABLE 2—ELUTION OF CEA (%) USING BATCH TECHNIQUE

Elution system	30 min P-300	30 min Seph 4B	60 min P-300	60 min Seph 4B	120 min P-300	120 min Seph 4B	240 min P-300	240 min Seph 4B	20 hr P-300	20 hr Seph 4B	44 hr P-300	44 hr Seph 4B	68 hr P-300	68 hr Seph 4B	92 hr P-300	92 hr Seph 4B
0.1 *M* acetate *p*H 4.0	1.0	–	1.0	0.1	7.3	1.0	6 8	1.9	10 5	3 3	35.0	–	32.4	–	32.5	–
0.1 *M* Gly-HCl *p*H 3.5	2.4	–	2.4	5.1	4.0	7.0	3 8	8.1	18 2	11.9	37.5	–	25.3	–	28.8	–
0.1 *M* Gly-HCl *p*H 3 0	7.2	–	8.3	16.0	21.3	18.5	22.8	20.6	43.1	24 4	55 6	–	49.5	–	53.4	–
0 1 *M* Gly-HCl *p*H 2 5	11.6	–	16.0	39.5	33.5	41 6	37 1	43.4	53 8	48 2	52.1	–	47.1	–	47.1	–
0.1 *M* Gly-HCl *p*H 2 0	22 7	–	26.5	54 8	28.0	57.4	39.3	56.8	40.8	61 2	57 4	–	58.1	–	58.1	–
0 1 *M* NaCl-HCl *p*H 1 4	30.7	–	30.6	84 1	38.1	83.8	38 9	85.9	59.1	89.8	58.3	–	64.2	–	61.2	–
3 *M* $MgCl_2$	2.0	–	6.4	41.6	17 1	50 8	26.1	58.1	41 9	82 2	55.5	–	54.3	–	63 5	–
3 *M* NaSCN	4 8	–	20 9	53.7	28 7	63 1	39.6	71.4	50.0	99.0	72.4	–	82.7	–	84.7	–

tized with radio-tagged homologous antibody. The unbound protein in the supernatant was then determined. The immunoadsorbent was exhaustively washed until no further protein could be determined in the wash fluid at 280 nm. The immunoadsorbent was then transferred to the chamber of the apparatus and washed several tim s with 0 1 *M* phosphate buffer *p*H 7.0 followed by successive aliquots of 50 ml of 0.1 *M* glycine-HCl buffer *p*H 3.5 to elute attached proteins. The latter step was repeated until the O.D. was less than 0.5 at 280 nm (12 elutions).

Purification of CEA :

58.2 mg of gamma fraction of homologous anti-CEA antiserum incorporated in biogel P-300 immunoadsorbent was incubated overnight at 45° with perchloric acid extract of colonic adenocarcinomatus tissue. Following incubation, the gel was thoroughly washed with 0.1 *M* ammonium acetate *p*H 6.25 and two washes of PBS. CEA was eluted with acid buffers and chaotropic ions.

Results

With a little practice the apparatus proved to be simple to operate. The amount of ligand recovered depended on a variety of factors, viz, amount immunoadsorbent used, avidity of the antiserum, length of incubation period of the ligand with the immunoadsorbent, etc. Contamination of eluted ligand by extraneous proteins varied from a total absence to moderate depending on a number of factors, chief of which was the duration and effectiveness of the saline washing cycle. When the optical density at 280 nm of the wash fluid approached zero, contamination was usually negligible but not invariably so.

It proved to be expedient to follow the saline wash with an acidic wash which at times eliminated contaminants released by the more acidic eluting fluid. When a protein copolymer was used as the immunoadsorbent, albumin and prealbumin in small quantities were continuously leached into the ligand eluting fluid so that it had to be removed by Sephadex gel chromatography.

The chief advantage of the apparatus described here lies in the ability of the operator to rapidly carry out sequential steps in the attachment, washing and elution of the ligand *in situ*, repeating the cycle as often as necessary to obtain the desired amount of ligand. The concentration of the ligand in the solution is immaterial since the latter binds to the immunoadsorbent, with the result that very dilute solutions can readily be used to saturate the polymer.

For large scale purification of a ligand, it is necessary to optimize the elution conditions. Results on the purification of IgG and CEA using acid buffers and chaotropic ions have been recorded in Tables 1 and 2 The numbers represent the percent of the total ligand initially bound to the immunoadsorbent.

Dissociation using acid buffers :

0.1 *M* acetate *p*H 4.0 and 0.1 *M* glycine-HCl *p*H 1 4 to 3.5 were used as the dissociating fluids. Recovery of IgG (Table 1) was 33.8% when *p*H 2.5 buffer was incubated for 1 hr with P-300 immunoadsorbent. Under similar conditions, Sephrose 4B gel yielded 56.8% Increase in the incubation time did not increase the yield but a lower *p*H increased the recovery as expected. Recovery from Sephrose 4B immunoadsorbent, in general, was greater than from P-300 as is evident from Tables 1 and 2. Results on the recovery of CEA (Table 2) were similar to that of IgG.

Dissociation using chaotropic ions :

Tables 1 and 2 delineate the use of 3 *M* $MgCl_2$ and 3 *M* NaSCN as eluents for human IgG and CEA. Sephrose 4B immunoadsorbent, in contact with the chaotropic ions for 3 hr, released 76.2 to 85% of the ligand (IgG), whereas under similar conditions P-300 complex yielded around 37%. Sephrose 4B complex, when incubated for 1 hr with either of the ions, yielded over 74%, whereas the recovery from P-300 complex was only around 22%. Recovery of CEA was similar to that of IgG. It is, however, interest-

ing to note that sodium thiocyanate recovered more CEA than $MgCl_2$.

Recovery using semi-automated affinity chromatography :

Results of previous experiments (Tables 1 and 2) helped set-up the final recovery experiments using semi-automated affinity technique. Table 3 presents two sets of data where 30 g and 50 g of immunoadsorbents were incubated with 10 ml of solution containing human antibody. Acid buffer *p*H 2.0 recovered 204 mg/ml of the ligand whereas with $MgCl_2$, the yield was 370.1. Sequential recoveries using different acid buffers and varying concentration of $MgCl_2$ are also recorded in Table 3. Purity of the antibody was checked by radial immunodiffusion (RID) and immunoelectrophoresis (IEP).

TABLE 3—ELUTION OF ANTIHUMAN ANTIBODY USING SEMIAUTOMATED TECHNIQUE

Elution system	Kappa light chain	Antihuman antibody (mg/ml)	
		Immunosorbent : 30 g	Immunosorbent : 50 g
Glycine-HCl (0.1 *M*, *p*H 3.0)	+	97 8	120 0
Glycine-HCl (0 1 *M*, *p*H 2.5)	++	163 2	204 3
Glycine-HCl (0.1 *M*, *p*H 2 0)	++	204 0	217.5
$MgCl_2$ (1 0 *M*)	+	102 2	127.5
$MgCl_2$ (2.0 *M*)	++	125 3	156.3
$MgCl_2$ (3 0 *M*)	+++	370.1	462 5

CEA and kappa light chains were also purified in similar manner. Recovery of CEA was 22 5 mg/ml and that of kappa light chain 16.' mg/ml. In another experiment, human IgG was purified using DEAE Sephadex. 50 ml of normal human serum yielded 10 mg of the immunoglobulin. Purity of these proteins were also confirmed by RID and IEP.

Binding capacity of polyacrylamide gels :

Table 4 records the binding capacity of Biogel P-60, P-200 and P-300, where gamma globulin was covalently attached to the gel matrix using glutaraldehyde. Results have also been represented graphically in Fig. 3. In successive experiments where IgG (gamma globulin) was covalently bonded to P-60,

TABLE 4—BINDING CAPACITY OF POLYACRYLAMIDE GEL TO GAMMA GLOBULINS

Gel	Wet weight of gel (g)	Gamma globulin (mg)	Gamma globulin attached (mg)*	Binding capacity P-60 : P-200 : P-300
P-60	2 8	11 52	1 61	
P-200	3 0	11.52	3.23	1 : 2 : 2.38
P-300	2.3	11.52	3 83	

* per wet weight (g) of gel.

P-200 and P-300, 4.0 mg of the protein could not saturate either of the gels (2 8 g of P-60, 3.0 g of P-200 and 2.3 g of P-300), 8.0 mg of IgG could saturate only P-60, whereas 11.5 mg of IgG saturated all the three gels. Capacity of the gels when calculated in terms of IgG/g was found to be in the ratio of 1 : 2 : 2.38 (Table 4) for P-60, P-200 and P-300, respectively. The capacity experiment aided in the establishment of three different affinity columns using P-60, P-200 and P-300 gels containing the same amount of antigen. On elution with 3 *M* NaSCN, 49.6% and 40.0% of the antibody was isolated in
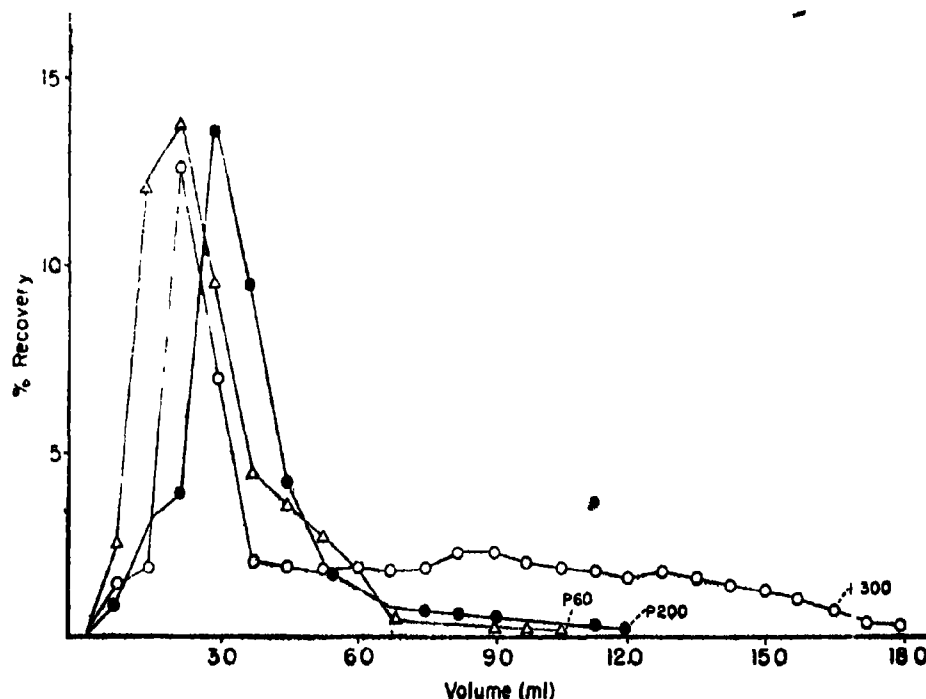
Fig. 3. Recovery of CEA with P-60, P-200 and P-300 immunoaffinity columns.

void volumes of P-60 and P-200, whereas only 24.5% was isolated in the void volume of P-300 and 27% in the later fractions (Fig. 3).

Comments and Conclusion

That the affinity type of adsorbtion and desorbtion applied to insolubilized immunoadsorbents is revolutionizing the purification of biospecific substances is attested to by the rapidly burgeoning mass of literature on the subject. Although the initial enthusiasm for this technique has been dampened somewhat by the realization that a number of shortcomings are inherent in the technique, particularly non-specific adsorbtion of contaminants, the deficiencies have been offset by expansion of the approach to different types of specimens. Because of the general utilitarianism and widespread use of affinity procedures, development of more rapid, semi-automated and automated techniques to reduce the expenditure of work and time associated with the procedure is of practical importance. The simple apparatus described in this communication provides the opportunity to effectively speed up the purification of substances on a preparative scale. With respect to the type of immunoadsorbent used, simple precipitation of the gamma fraction of a monospecific antiserum by 10% polyethylene glycol (PEG) followed by polymerization with glutaraldehyde provides a rapid, simple procedure for preparing efficient immunoadsorbents which are often preferable and more economical than commercially supplied pre-sensitized gels. Also, less complete but more frequent elution of a substance coupled to a ligand are more efficient than prolonged elution[8]. Our results have shown that ten to twenty elutions are required to release the major portion of a bound substance from its ligand. Finally, it is pertinent to point out that the apparatus may be used to advantage for purifying substances by the ion-exchange principle as described for IgG.

Although there is little doubt that sophisticated, automated equipment and techniques will be developed in the near future to deal with the purification of substances by the affinity principle, the simple approach described above is immediately available for use. Recovery results of all the elutions have been reported in Tables 1, 2, 3 and Fig. 3. As expected, recovery is higher at a lower pH but it is also evident that chaotropic ions ($MgCl_2$, NaSCN) dissolve and dissociate antigen-antibody complexes. Dissociation of complexes with $MgCl_2$, NaSCN occurs rapidly in contrast with acid dissociation, for which contact times of several hr are needed for a significant recovery. The protein immunospecifically purified by the chaotropic ions retained its ability to combine with ligand to form soluble and insoluble complexes. In $3M$ NaSCN and $3M$ $MgCl_2$, the concentration used for protein purification, no significant amount of irreversible gross structural changes was noted in any of the proteins. Saussure and Dandliker[10] observed that at 4.5 M and above, SCN caused changes in the sedimentation behaviour of gamma globulin, antigen and complexes. These changes were reversible by dialysis.

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Biochemical Fuel Cells

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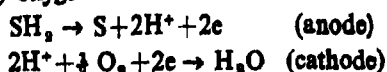
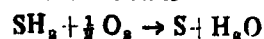
The need for tapping sources of energy other than the conventional ones necessitates the development of biochemical fuel cells in which a large variety of biomass can be used as fuels. The present status of biochemical fuel cells is reviewed. The main drawback of such fuel cell is the slow transfer of electrons from the substrate to the electrodes. Both experimental and theoretical studies have been started to understand the basic processes underlying the electron transfer in such systems. Preliminary results of such studies are very encouraging and further work in the area is in progress

OUR energy demands are increasing and in view of the sky-rocketting price of petroleum products and the depletion of natural resources, it is becoming increasingly clear that sources of energy other than the conventional ones have to be tapped to meet the situation. The awareness of this situation and the possibilities of finding new sources of energy in the context of our own country have been highlighted recently[1].

The main conventional sources of energy today are fossil fuels, hydroelectricity and nuclear energy. Each of these has its own limitations and associated hazards. The devices using fossil fuels like coal, gasoline, diesel etc. generally operate through a heat cycle (Carnot cycle). The fuel is oxidised (burnt) and the thermal energy produced is utilized either to drive mechanical engines or is converted into electrical energy. The efficiencies of such devices are, however, limited by Carnot cycle and one obtains efficiency upto about 20%. To increase the efficiency of these systems, one has to go to higher operating temperatures which is again restricted by technological difficulties. It is, therefore, logical to look for devices which can directly convert chemical energy into electrical energy. This is, basically, accomplished in a fuel cell and the efficiency in fuel cell can be as high as 50%.

A fuel cell (FC) is an electrochemical device in which part of the energy derived from chemical reaction maintained by a continuous supply of chemical reactants is converted into electrical energy. In a biochemical fuel cell (BFC) the oxidation (burning) of bioorganic materials (fuels) is catalysed by specific enzymes. The electrochemical reactions usually take place with air as oxidant at the cathode while the enzymes catalyse the oxidation of bioorganic material at the anode. In general, one uses hydrogen or hydrogen rich fuels (SH_2) such as methane, methanol, ethanol, carbohydrates, etc. The energy producing reaction is the oxidation of hydrogen by oxygen

$$SH_2 \rightarrow S+2H^+ +2e \quad \text{(anode)}$$
$$2H^+ + \tfrac{1}{2} O_2 + 2e \rightarrow H_2O \quad \text{(cathode)}$$

Such that the net reaction is

$$SH_2 + \tfrac{1}{2} O_2 \rightarrow S + H_2O$$

Each cell based on above reaction can produce few hundred watts of d.c. power. In a fuel cell power plant, several such cells can be stacked together.

Historically, the concept of biochemical fuel cell is not new. As far back as in 1911, Potter[2] observed that "disintegration of organic compounds is accompanied by the liberation of electrical energy". He constructed the first biochemical fuel cell and obtained voltages upto 0.35 volts from yeast-glucose systems. Cohen[3] in 1931 did more precise work on generation of electrical energy from various cultures and sterile media. There was then a period of relatively low activity until early 1960's when the interest in biochemical fuel cells revived[4-6]. This activity was also initiated by several governmental and non-governmental agencies in U. S. like NASA, Magna Corpn., GEC, Ford Motors, Marquardt Corpn., Electron Molecule Research Inc., General Scientific Corpn., etc. but most of the outcome has remained classified for obvious reasons.

Design af biochemical fuel cells :

Fuel cells are different from batteries. This is due to the fact that fuel cells can supply power intermittently (reactants are fed and products removed continuously) and that the electrodes are not consumed Most of the inorganic fuel cells use either highly alkaline (30–80% KOH) or highly acidic electrolyte media[7], oxidation of hydrocarbon, methanol, ammonia or hydrogen as fuels and relatively expensive metallic electrodes to stand highly corrosive conditions. One has also to use high temperature and pressure because the fuels have a high activation energy and do not oxidize under ambient conditions. It is here that the use of specific enzymes (or bacteria) helps by lowering the barrier to chemical reactions and thus making the electrochemical reactions feasible under milder conditions. It has been estimated that for a direct electron transfer process, a current of the order of 10^{17} amp (at 1 volt) can be delivered by using 1 kg of enzyme[8]. For all practical purposes even a

millionth of the above current (10^{11} amp for 1 kg of pure enzyme) will be of valuable commercial application.

In the direct biochemical fuel cell, the oxidation of raw fuels such as starch, carbohydrate or protein is achieved with the help of bacteria via a stepwise transfer of protons involving several classes of enzymes and coenzymes (such as NAD), flavoprotein, cytochromes and coenzymes Q provided by the bacteria. The combustion rate in such cells is low since the reactions have to be carried out in a narrow range of *p*H and temperature

The indirect biochemical cell works in two steps The first step involves the conversion of raw fuel into simpler biochemical end products such as H_2, CH_4, NH_3, CH_3OH, etc. with the help of suitable bacteria. The secondary fuel, thus generated, is transferred to a second compartment where the electrical power is generated in one step enzymatic oxidation of such products. While such systems are quite convenient and easier to optimize, there is an additional engineering problem which is the transfer of secondary fuel to the fuel cell compartment. Both types of biochemical fuel cells have been reported in the literature[4-8,9-13].

Many organic waste materials or natural sources can be used as fuel in biochemical fuel cells. Sisler[4] reported a biochemical fuel cell which worked on undiluted sea water (which contains plant-carbohydrates synthesized by marine algae) through sulphate reducing bacteria, *Desulfovibrio desulfuricans* and obtained approx 0.5 volt with a current output of 1 milliamp. Colichman[8] extended Sisler's study to a much broader application by utilizing various bio-fuels and obtained a better power level with fresh mushrooms serving as fuel by the catabolic action of *Desulfovibrio desulfuricans*. Many other biochemical fuel cells have been reported and some of these are :

(i) hydrocarbon (natural gas) as fuel and hydrocarbon oxidizing bacteria as catalyst[10,14],

(ii) urea (urine) as fuel and urease (*Bacillus pasterii*) as catalyst[9],

(iii) glucose as fuel and glucose oxidase as catalyst[11],

(iv) organic materials and hydrogenase to produce H_2 gas for use in the indirect fuel cells[12].

Design difficulties :

There are several difficulties in designing biochemical fuel cells which provide challenges to technologists as well as to basic scientists. These systems have intrinsically low voltages (a typical redox system has voltage ~1V) and hence they have to operate at high current densities to be of any practical use. The following problems arise in operating the systems at high current densities :

(i) The transfer of electrons from the enzyme-fuel system to electrode is rather slow. At present there is no obvious solution to this problem although several groups are interested in electron transfer from biological macromolecules to conductors,

(ii) The electrolyte should have a low electrical resistance and the extreme *p*H conditions or salt concentrations which are needed to increase the electrical conductance are injurious to the bacterial system. This problem can be overcome by the use of indirect cell system,

(iii) The electrodes have to be designed from expensive materials and they have relatively short life due to corrosion and bacterial contamination. This problem again can be avoided by the use of indirect fuel cell operating on pure enzyme systems,

(iv) One should be able to produce stable enzymes with sufficient kinetic activity and in bulk quantity at relatively low cost. Several enzymes are now commercially available and their prices are also decreasing.

Coenzyme immobilised anodes for BFC :

Many biological oxidation-reduction reactions utilise a coenzyme as a proton and electron carrier which functions in conjunction with a covalently linked enzyme specific for the substrate used as fuel. A typical example is glucose oxidase which uses flavin adenine dinucleotide (FAD) as a coenzyme in the oxidation of glucose to gluconic acid. The

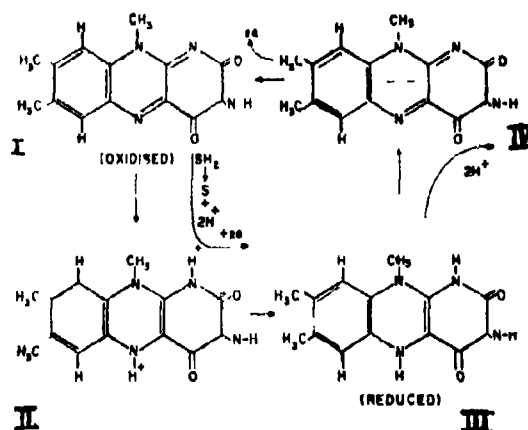



Fig. 1. The oxidation-reduction cycle of FAD which involves transfer of two protons and two electrons. Electrons are transferred to the electrode in step IV→I while the oxidised form is enzymatically reduced to $FADH_2$ (III) by the substrate which releases two protons and two electrons. The protons released in step III→IV are absorbed by the buffer and transported to cathode compartment.

complete redox cycle of this coenzyme is schematically represented in Fig. 1. The oxidation of fuel (SH_2) in presence of the enzyme (E) liberate two protons and two electrons. These can be taken up by the oxidised FAD (I) to give $FADH_2$ (III). Likewise, the regeneration of oxidised form of FAD involves sequential release of two protons (IV) and two electrons (I). In the fuel cell (Fig. 2), the two protons have to be transported from the anode compartment to the cathode. Protons being water soluble, they can easily pass into the aqueous phase from the coenzyme and then to the cathode compart-

ment. On the other hand, the two electrons have to be passed on to the electrode by a suitable mechanism. Our approach to circumvent this problem is based on immobilisation of FAD on graphite through semiconducting linkages such that an electron transport bridge can be established for a direct passage of electrons to the graphite anode. Such an electrode can then serve as a bioanode. In conjunction with an oxygen electrode, the biochemical fuel cell can yield voltages of 1 V or higher[15].

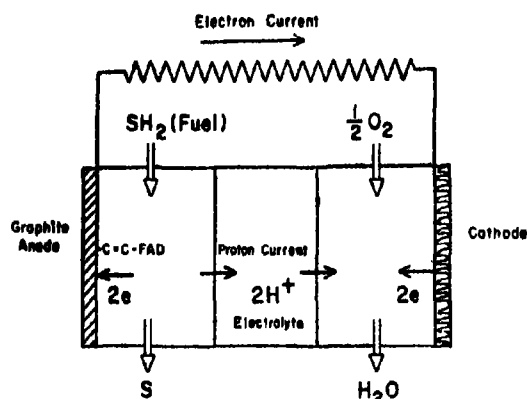



Fig. 2 The conceptual drawing of a biochemical fuel cell based on FAD. The FAD immobilized on graphite is used as a cathode. Protons are transferred from the anodic to cathodic compartment giving rise to an internal proton current as opposed to electron current in the external circuit.

We have made systematic molecular orbital studies of the electron-flow diagrams of riboflavin during its redox cycle. The calculations show, as expected for aromatic ring systems, that the charge distributions in all the four states of FAD are highly delocalised. However, in the electron release step IV→I the largest electron flux occurs from the two carbonyl groups. These then should serve as ideal sites for immobilising flavin on graphite through semiconducting linkages. The chemical steps involved in this process involves creating active centres on the graphite surface which can then be condensed with FAD to form covalent linkages between the electrode and the coenzyme. Cyclic voltamograms of the modified electrode show that FAD is active and undergoes the expected redox cycles. Further work on the design of BFC based on this approach is in progress.

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Metal Ammine Formation in Solution. Part–XXIII : The Nickel(II)-Mono- and Diethanolamine Systems

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This paper reports a potentiometric and spectrophotometric study of the nickel(II)-mono- and diethanolamine systems. The metal ammine formation was studied by glass electrode measurements in 2 M amHClO$_4$ and 0 5 M (amH, Na) ClO$_4$ solutions at 25° and the stability constants determined. The effect of the partly coordinated alcohol groups on the stability constants is considerable. The nickel(II) ion shows little tendency to bind more than two diethanolamine and three monoethanolamine molecules. Spectrophotometric measurements show that aqueous nickel(II) solutions with more than 60 weight per cent of monoethanolamine and pH > 12 have unchanged absorption on further addition of amine. These solutions are presumed to contain a deprotonated species with less than four amino groups bound to nickel.

IN continuation of a paper by Agarwala and Bjerrum[1] on the nickel(II)-triethanolamine system the stability constants of the nickel(II)-mono- and diethanolamine complexes under the same experimental conditions are determined in the present paper. Potentiometric measurements of these systems have previously been made by the Russian authors[2-4] and spectrophotometric measurements in alcoholic and aqueous solutions have also been performed by them[5-7]. In the present paper spectrophotometric measurements have been made in 2 M ethanolammonium perchlorate solutions and in strong aqueous monoethanolamine solutions with up to 92 weight per cent of the amine.

Experimental

Reagents and solutions : All reagents were of analytical grade. The monoethanolamine (Fluca, puriss) was distilled under atmospheric pressure and the main fraction boiling at 165° was used without further purification. The diethanolamine (Fluca, puriss) was distilled at ~10 mm Hg and the main fraction boiling at 160-163° was used without further purification The various solutions were prepared in volumetric flasks by weighing or pipetting from stock solutions. [illegible] 50 M stock solution of the ethanolammonium perchlorate was prepared by neutralizing 1 liter 5.00 M HClO$_4$ with the amine and diluting to 2 liters. Complete equivalence between amine and perchloric acid was ensured as described earlier[8] All mass action constants are concentration constants (mol / liter units) in the applied medium. Other experimental details were the same as in the preceding paper[1].

Discussion of pH measurements : The results of some of the measured solutions are shown in Table 1. All concentrations are in M/l and the ligand number

TABLE 1—SELECTED RESULTS OF GLASS ELECTRODE MEASUREMENTS OF NICKEL(II)-MONO- AND DIETHANOLAMINE PERCHLORATE SOLUTIONS AT 25°

No.	C_{meaH}	C_{Na}	C_{Ni}	C_{mea}	p[mea]	pH	n
1	0.50	0	0.01046	0 00397	3.514	6.326	0.350
2	0.50	0	0 01046	0.0159	2.634	7.206	1.298
3	0.50	0	0.01046	0 0496	1.644	8.196	2 572
4	0.50	0	0 01063	0.0992	1.168	8.672	2.940
5	2.00	0	0 1154	0 0498	3 595	5.905	0.429
6[a]	2.00	0	0.1154	0 1332	2 990	6.510	1 145
7[b]	2.00	0	0 1154	0.1663	2.814	6.686	1.428
8	2.00	0	0.1154	0 3322	1 637	7.863	2.679
9	2.00	0	0.1154	0 4155	1.187	8.313	3.037
	C_{deaH}	C_{Na}	C_{Ni}	C_{dea}	p[dea]	pH	$\bar{n}$
10	0.100	0.400	0 0115	0 00536	2.960	5.980	0.370
11	0.100	0.400	0.0115	0.00965	2.631	7.309	0.636
12	0.100	0.400	0.0115	0 0268	1 924	8.016	1.296
13	0.100	0.400	0.0115	0 0386	1.680	8.260	1.530
14	0.50	0	0.0115	0.00643	2.858	6.372	0.438
15	0.50	0	0.0115	0 0107	2.570	6.660	0.697
16	2.00	0	0.0577	0.0215	3 380	5.650	0.365
17	2.00	0	0.0577	0 0322	3.107	5.923	0.545
18	2.00	0	0.0577	0.0859	2.248	6.782	1.391
19	2.00	0	0.0577	0.1502	1.409	7.621	1.927

[a] Calcd. $\alpha_0 = 0.22$, $\alpha_1 = 0.47$, $\alpha_2 = 0.29$, $\alpha_3 = 0.03$, $\bar{n} = 1.14$
[b] Calcd. $\alpha_0 = 0.13$, $\alpha_1 = 0.42$, $\alpha_2 = 0.39$, $\alpha_3 = 0.06$, $\bar{n} = 1\ 38$

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is calculated from the expression

$$\bar{n} = (C_{a,n} - [am] + [H^+])/C_{Ni}$$

where C_X represents the stoichiometric concentration of the species X. In Fig. 1 the formation curves are plotted for the nickel(II)-monoethanolamine (mea) and diethanolamine (dea) systems in 0.5 M (amH, Na)ClO_4 and 2 M am$HClO_4$ solutions. For purposes of comparison, the curves determined by Agarwala and Bjerrum are also drawn for the triethanolamine system and those for the nickel(II)-ammonia system in 0.5 M and 2 M $NHNO_3$ at 25°[6]. The ethanolammonium concentrations are varied in the 0.5 M (amH, Na)ClO_4 solutions as seen from Table 1 and indicated by the signs of the points in Fig. 1. Contrary to the triethanolamine system[1], the influence of changing the $meaH^+$ and $deaH^+$ concentrations is found to be negligible. A change in C_{Ni}, from 0.005 to ~0.1 M also has no influence on the formation curves within the uncertainty of the experiments. It can, therefore, be concluded that the metal ammine formation in the Ni(II)-mea and Ni(II)-dea systems is not interfered by hydrolysis and polymerization reactions.

Fig. 1. Formation curves ($\bar{n}$ vs p[am]) at 25° for the three nickel(II)-ethanolamines Experimental and calculated values for nickel(II) mono- and diethanolamine in 0.5 M (amH,Na)ClO_4 and 2 M am$HClO_4$ compared with the calculated curve for nickel(II)-triethanolamine in 0.5 M and 2 M tea$HClO_4$[1] and with the nickel(II)-ammonia system in 0.5 M and 2 M NH_4NO_3 at 25°[6]. Signs used for 2 M am$HClO_4$: ○ (C_{Ni} ~0.01 – 0.02 M), ● (C_{Ni} ~0.04 – 0.1 M), and ◑ (C_{Ni} ~0.005 M). Signs for 0.5 M am$HClO_4$: □ (C_{Ni} ~0.01 – 0.02 M), ◘ (C_{Ni} ~0.04 M) and ◧ (C_{Ni} ~0.005 M) and for 0.1 M am$HClO_4$, 0.4 $NaClO_4$: △ (C_{Ni} ~0.01 – 0.02 M).

The full drawn curves in Fig. 1 are calculated on the basis of the estimated constants shown in Table 2. The constants determined by the Russian authors[8,9,10] are also shown for comparison. The values determined by Sychev and Gerbeleu for the Ni(II)-mea[9] and Ni(II)-tea[10] systems are in reasonably good agreement with our values apart from their value for K_2 in the Ni(II)-tea system which should have been corrected for hydrolysis. On the other hand, the values presented by Sklenskaya and Karapet-yants[8] for all three ethanolamines are not reliable.

The amines are bound to the metal through the nitrogen atom but it is obvious that the alcohol groups also take part in the complex formation. The large values of the ratios between successive constants and the decreasing number of ligands taken up with increasing number of alcohol groups involved show directly that chelation plays a role. It is therefore reasonable to assume that $Ni(mea)_3^{2+}$ and $Ni(dea)_2^{2+}$ to some extent, are octahedral complexes with three chelate bound, respectively two tridentate bound ligands. The small tendency of these complexes to take up further ligands and of $Nitea^{2+}$ to take up a second ligand supports these assumptions. However, the coordination of the alcohol groups must be weak for it had no observable effect on the enthalpy changes. Sychev and

Table 2—The Determined Stability Constants for the Three Nickel(II)-Ethanolamine Systems and the Protonation Constants of the Amines in Ethanolammonium Salt Solutions at 25°

$$K_n = \frac{[Ni(am)_n]}{[Ni(am)_{n-1}][am]}, \quad \beta_n = \frac{[Ni(am)_n]}{[Ni][am]^n}$$

	Mea			Dea			Tea		
	0.4[c]	0.5[a]	2[a]M	0.43[e]	0.5[a]	2[a]M	0.5[d]	0.5[b]	2[b]M
pK_{amH}	–	9.54	9.80	9.09	8.93	9.32	–	7.90	8.32
$\log K_1$	3.06	3.12	3.32	3.31	2.60	3.00	2.27	2.85	3.42
$\log K_2$	2.46	2.56	2.78	2.13	1.87	2.27	0.82	0.14	0.87
$\log K_3$	1.43	1.80	2.00	1.42 ?	–	–		—	–
$\log K_4$	–	(0.32)	(0.40)		–	–		—	–
$\log \beta_2$	5.52	5.68	6.10		4.47	5.27		2.99	4.29
$\log \beta_3$	6.95	7.48	8.10		–	–			–
$\log \beta_4$	–	(7.80)	(8.50)		–	–		—	–

[a] Values determined in this paper.
[b] Values determined by Agarwala and Bjerrum[1] in 0.5 M (teaH, Na)ClO_4 and 2 M tea$HClO_4$.
[c] Values determined by Sychev and Gerbeleu[9] in 0.4 M (meaH, K)NO_3 at 25°.
[d] Values determined by Sychev, Gerbeleu and Migal[10] in 0.5 M (teaH, K)NO_3 at 25°.
[e] Values determined by Sklenskaya and Karapet-yants[8] in 0.43 M (deaH, K)NO_3 at 25°.

Gerbeleu[9,10] have determined the enthalpy changes in the Ni(II)-mea system and found for the uptake of the first three ligands $-\Delta H_1=3.35$, $-\Delta H_2=3.90$ and $-\Delta H_3=2.60$ kcal/mol, and for the first ligand in the Ni(II)-tea system $-\Delta H_1=3.86$ kcal/mol. These values are of the same order as the average value 3.5. kcal/mol for the uptake of an NH_3-molecule in the Ni(II), NH_3 system[9,11].

Finally it should be noticed that the influence of the ethanolammonium concentrations on pK_{amH} and the stability constants is unusually high and increases in the order tea>dea>mea>NH_3 (cf. Fig. 1 and Table 2).

Discussion of Ni(II)-mea spectra : Fig. 2 shows the absorption (ϵ, λ)-curves in the visible range for Ni(II)-mea solutions in 2 *M* meaHClO$_4$ (curves 4-7) with $\bar{n}$ varying from 0 to 1.42 On the basis of these data the position of the absorption maximum
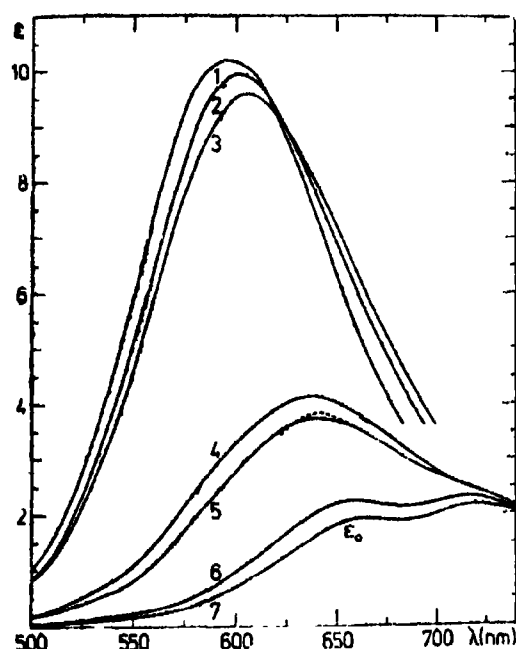
Fig. 2. Spectra (ϵ, λ) of nickel(II)-monoethanolamine perchlorate solutions at 22-23° The composition of the solutions are as follows

1 $C_{Ni}=0.0418$ *M*, $C_{mea}=15.29$ *M* (92%)
2 $C_{Ni}=0.0418$ *M*, $C_{mea}=5.32$ *M*
3. $C_{Ni}=0.0418$ *M*, $C_{mea}=1.33$ *M*
4. Sol. 7 in Table 1. $\bar{n}=1.428$.
5. Sol. 6 in Table 1. $\bar{n}=1.145$
6. $C_{meaH}=2.00$, $C_{Ni}=0.1154$, $C_{mea}=0.0200$, $\bar{n}=0.173$.
7 $C_{meaH}=2.00$, $C_{Ni}=0.1154$, pH~2, $\bar{n}=0$.
Estimated for ϵ_1 - - - - - -

of the mono-amine complex is estimated to be $\lambda_{max}(\epsilon_1)=642$ nm. This is a blue shift of 18 nm compared to that of the aqua nickel(II) ion with $\lambda_{max}(\epsilon_0)=660$ nm. A blue shift of this magnitude agrees well with what is found in the Ni(II)-tea[1] and in the Ni(II)-NH_3 system[9].

The curves 1-3 in Fig. 2 show the absorption spectra of aqueous monoethanolamine nickel(II) perchlorate solutions with $C_{mea}=15.29$, 5.32 and 1.33 M/*l*. respectively. Solutions with $C_{mea}=10.64$ and 11.97 M/*l* were also measured but their absorption curves were so close to that of the limiting curve with λ_{max} at 595 nm (and 92 weight per cent of monoethanolamine) that they are not plotted in the figure. Measurements were also made of two solutions with $C_{mea}\sim10$ M/*l* and added strong base: $C_{NaOH}=0.04$ and 0 4 M/*l* The first solution had practically the same λ_{max} and ϵ_{max} as the limiting curve, but for the stronger basic solution a small red shift of λ_{max} to 605 nm and a decrease of ϵ_{max} from 10.0 to 8 8 were observed. The blue shift of λ_{max} from the aqua nickel ion to λ_{max} of the limiting curve is therefore found to be 660-595≃65 nm. From this estimate it can be concluded that at the most 65/18≃3.6 amine groups can be coordinated to the nickel ion. In these solutions with pH>12 it is reasonable to assume that deprotonated species such as $Ni(mea')_3^-$ are dominating. In solutions of higher basicity, it is possible that the amine ligands are exchanged with hydroxyl ions. The small red shift observed when the added concentration of NaOH is increased from 0.04 to 0.4 M/*l* seems to support this assumption.

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The Rare Earths. Part—XCII : Chelating Tendencies of 1-Methoxy-2,4-pentanedione

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Chelating tendencies of 1-methoxy-2,4-pentanedione toward tervalent lanthanide ions were measured in 50% (v/v) dioxane-water media, and thermodynamic formation constants were obtained. In addition, enthalpy values were obtained by thermometric titrations using the same systems. The data obtained support the interpretation of an expanded solvation sphere through the lanthanide series. The use of the mixed solvent system permitted third formation constants to be obtained without concomitant problems of precipitation, although the possibility of dioxane coordination in the solvent sphere exists. Relatively large values of entropy of formation for the overall chelation processes imply an increase in the hydration number from lanthanum through lutetium. Anomalies in chelating tendencies at gadolinium and erbium are difficult to explain unambiguously. The values may indicate a type of cross-over point at which solvent-metal and ligand-metal interactions result in a break in the apparent continuity of the ligand-metal process through the series.

MANY studies of the chelating tendencies of lanthanide ions have involved a single chelating agent associated with a single metal ion, e g., lanthanide-aminepolycarboxylate chelates and studies of the chelating tendencies of β-diketones have been limited[1] despite the advantages that these systems may offer. The present study was initiated to permit comparison of the effects of oxygen-oxygen coordination versus oxygen-nitrogen coordination, to make a comparison of inductive and steric effects of various substituents (R, R′ and R″) in RCOCH(R″)-COR′$^-$ of the β-diketonate chelating agent.

Some experimental difficulties and advantages were anticipated. A mixed-solvent system was required, because of the insolubilities of the metal chelates, $Ln(RCOCH_2COR')_3$, in water. The use of dioxane-water systems, however, for obtaining thermodynamic formation constants has been well established[1]. In addition, the study of lanthanide-acetylacetonate complexes made by Fernelius and co-workers[2] indicated that complexes of reasonable stabilities could be obtained.

It was also, evident that 1-methoxy-2,4-pentanedione could offer the advantage of reasonable stability plus enhanced solubilities. Finally, the possibility of obtaining three stepwise equilibrium constants was attractive for several obvious reasons.

The use of enthalpy titration data seemed advisable for evaluating $\triangle H_n$, the change in enthalpy associated with a given stepwise chelation process, because the equilibria were established sufficiently rapidly and because data were not available to permit thermodynamic formation constants to be determined for dioxane-water media at temperatures other than 30°.

Experimental

Materials : 1-Methoxy-2,4-pentanedione from a commercial source was fractionally distilled under vacuum (52°/ 1 mm Hg), n_D^{20} 1.4590 obs ; 1.4590 reported[3] Perchlorate solutions : solutions of scandium, yttrium and lanthanide metal perchlorates were prepared from weighed quantities of oxides (99+% purity) by treatment with stoichiometric amounts of perchloric acid (G. F. Smith Chemical Co. ; diluted and standardized to 0.1000 M). All perchlorate salt solutions were standardized titrimetrically using xylenolorange as an indicator[4]. The usual precautions were taken in preparing dioxane and water[5].

Dissociation constants were determined in 50% dioxane-water, using tetramethylammonium hydroxide, as described elsewhere[1].

Formation constants : Titration solutions consisted of 5×10^{-3} M chelating agent and 4×10^{-4} M tervalent metal perchlorate in appropriate dioxane-water solutions to give 50% (v/v) contained in a four-necked titration flask immersed in a bath maintained at 30.00±0 02°. The procedure used in the titration is described elsewhere[1,5,6].

Enthalpy titrations : The enthalpy titration system consisted of five components : (1) a constant-temperature system, a Pyrex ball jar constant-temperature bath contained within a 350-L constant-temperature water bath, which resulted in the inner

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bath being stabilized to within ± 0.001°; (2) a titrant delivery system, which consisted of a Sargent model "C" constant-rate buret; (3) a titration cell, which consisted of a Dewar flask constructed from a 60/50 outer joint with a total volume of about 200 ml; (4) a heating circuit; and (5) a cell-temperature monitor system. Full details are provided elsewhere[6].

The enthalpy titration involved a continuous-addition technique: a 100.0 ± 0.1 ml sample of metal perchlorate and chelating agent in appropriate solvents (50 vol% dioxane-water) was placed in the cell and, following thermal equilibration, was treated by the continuous addition of titrant (1.0 *M* KOH). The temperature evolved was recorded on a strip chart as a thermogram, a time-dependent curve which represents the temperature of the calorimeter at any instant of time, relative to the initial temperature. A number of corrections and calibrations were made, including correction for the cooling effect due to entering solvent, calibration of the titration cell, calibration of the strip chart to temperature, evaluation of the heat capacities of the solvents, determination of the heat of ionization of the chelating agent, calculations of concentrations of the species initially and at a given time, t_i, correction of species distributions as a function of ionic strength and, finally, calculation of the enthalpies for the stepwise equilibria. The detailed descriptions of these treatments, together with the computer programs which effect the calculations of the heat of complex-ion formation, are presented elsewhere[6].

Results

Thermodynamic parameters for 1-methoxy-2,4-pentanedione: Typically, the pK_D value of a β-diketone is a linear function of the mole fraction of dioxane (N_2) in a dioxane-water solution, and the same was true in this study [$pK_D = 7.36 \pm 0.11 + (10.72 \pm 0.43) N_2$]. A polynomial least-squares treatment gives a better fit for the data, but either plot shows the increase in pK_D with a decrease in the dipole moment of the solvent. At $N_2 = 0.173$ (50 vol% dioxane), the values of the thermodynamic constants are ΔG^0_{i}- = 13.20 ± 0.01 kcal/mole; ΔH^0_{i}- = 0.99 ± 0.08 kcal/mole; and ΔS^0_{i}- = −40.3 ± 0.1 e.u. at 30.0 ± 0.01°. These values indicate that ionization of the chelating agent is primarily an entropy controlled process. Since ionization diminishes the entropy of the system, ionization is favored in higher dielectric solvents (lower values of N_2).

Other observations support this contention. Kido and Fernelius[7] observed little change in $\Delta H_{ionization}$ as a function of N_2. This and the observations of the present study indicate that the bonding energy differences remain fairly consistent with N_2.

Several structural implications also result from these parameters. First, the hydrogen ion must form nearly identical aggregations regardless of N_2 in the range studied. Also, the bulk solvent aggregation must be substantially diminished as the mole fraction of dioxane increases. Finally, water molecules remain the principal coordinating solvent species, and the dioxane molecules primarily affect the bulk solution properties. The importance of this view in extrapolating to a metal ion system is evident. Another supporting observation: the heat capacity of 50% (v/v) dioxane-water was determined to be 0.75 cal/ml-°C, whereas the value of pure water is 1.0 cal/ml-°C, at 30°, which is interpreted as indicating less aggregation in the mixed-solvent medium.

Formation constants for selected lanthanide ions in different dioxane-water mixtures:

Thermodynamic formation constants, as log K_n, were evaluated at four different mole fractions of dioxane in dioxane-water mixtures. Pertinent results are listed in Table 1.

An ionic relationship proposed by Born [log K=C(1−1/D)] was tested using the data in Table 1 and deviations from linearity were observed for all plots when N_2 is less than about 0.1, although the degree of non-linearity is not substantial. A substantial deviation in linearity implies that either the metal ion solvation does not remain constant from one solvent system to another or that covalency

TABLE 1—THERMODYNAMIC FORMATION CONSTANTS OF La^{3+}, Gd^{3+} AND Lu^{3+}-1-METHOXY-2,4-PENTANEDIONE CHELATES AT SELECTED N_2 VALUES AT 30.00±0.02°

N_2		0.0825 (30%)[b]		0.1735 (50%)[b]		0.2805 (65%)[b]		0.3864 (75%)[b]	
M^{3+}	i	log K_i	R_i^a	log K_i	R_i^a	log K_i	R_i^a	log K_i	R_i^a
La^{3+}	1	6.191	0.712	7.419	0.779	8.804	0.825	10.004	0.838
	2	4.675	0.537	5.828	0.612	7.267	0.681	8.496	0.711
	3	3.866	0.444	4.662	0.490	5.819	0.545	6.990	0.585
Gd^{3+}	1	7.113	0.818	8.348	0.877	9.678	0.907	11.048	0.925
	2	5.456	0.627	6.595	0.693	8.037	0.753	9.394	0.787
	3	4.206	0.483	4.898	0.515	5.985	0.561	7.329	0.614
Lu^{3+}	1	7.354	0.845	8.536	0.897	9.747	0.912	11.271	0.944
	2	5.715	0.657	6.795	0.714	8.339	0.782	9.614	0.805
	3	4.328	0.497	5.025	0.528	6.326	0.593	7.623	0.638
D[c]		51.38		33.85		21.77		14.68	

[a] $R_i = \log K_i / p^TK_a$.

[b] (XX%) represents XX% (volume dioxane)/(volume dioxane + volume water).

[c] The symbol *D* represents the solvent dielectric constant of the solvent system given at the top of the column.

exists in the metal-to-ligand bonding. Considering that the degree of deviation is small, we are led to the conclusion that there may not be a substantial change in the inner coordination sphere of solvated lanthanide ions in dioxane-water mixtures as compared with water as a solvent. The data for log K_3 for gadolinium show a notably linear Born plot; but whether this indicates a remarkably different process in comparison with those for lanthanum or lutetium remains uncertain, considering the small deviation from linearity. These results also indicated that studies using 50% (v/v) dioxane-water would provide results that would be representative of most mixtures (with N_2 above 0.1).

Thermodynamic constants for chelating tendencies of lanthanide ions :

Pertinent data are summarized in Tables 2-4. The results can be considered in order.

The values of ΔG_i° are plotted in Fig. 1 using the data from Table 2. When this is done, a distinct break appears at gadolinium for the first, second, and perhaps, the third chelation process. Also, such a plot reveals that ΔG_3° is anomalous for lanthanum; otherwise results are consistent with what others have found for other systems including the observation of a so-called "gadolinium break". In addition, the magnitude of the overall process, ΔG_{1-3}, is similar to the values obtained for other lanthanide complexes, e.g., 25 to 28 kcal/mole for $La^{3+}-Lu^{3+}$ versus 22-28 kcal/mole for DCTA complexes[8,9]. It must be recognized, however, that formation constants of complexes of EDTA and DCTA were determined in 0.1 *M* KNO_3, whereas the data for the β-diketone (Table 2) were obtained for 50% dioxane-water.

A similar problem occurs when the chelating tendencies of 1-methoxy-2,4-pentanedione toward lanthanide metal ions are compared with those of 2,4-pentanedione. The former were evaluated for 50% dioxane-water and the latter[2a] for dilute aqueous solutions at an ionic strength of 0 1. The available data clearly show the greater stabilities of the 1-methoxy-2,4-pentanedione complexes (log β_3= *ca* 20) relative to those of 2,4-pentanedione (log β_3=*ca* 11-12)[2a]. A more reasonable comparison may result if the pK_D values are compared: the values for N_2=0.173 are 10.37 for 2,4-pentanedione[10] and 9 52 for 1-methoxy-2,4-pentanedione If the values of log K parallel the pK_D values for closely related β-diketones as has been observed previously[11], then the complexes of 2,4-pentanedione should be somewhat more stable than those of 1-methoxy-2,4-pentanedione.

Fig. 1. Gibbs free energy of formation, ΔG', Kcal/mole, as a function of atomic number, Z, for 1-methoxy-2,4-pentanedione chelates of the lanthanides. The value of *i* is *1* for ○, *2* for ◐ and *3* for ⊖. The position of yttrium in the series is indicated by the symbol △. The size of the circles approximates the standard deviation of the value.

TABLE 2—FREE ENERGY OF FORMATION OF Ln^{3+}-1-METHOXY-2,4-PENTANEDIONE CHELATES IN 50 0 (v/v) % DIOXANE-WATER MEDIUM AT 30.00±0.01°

Z	M^{3+}	$-\Delta G^\circ_1$ Kcal/mole	$-\Delta G^\circ_2$ Kcal/mole	$-\Delta G^\circ_3$ Kcal/mole	$-\Delta G^\circ_{1-2}$ Kcal/mole	$-\Delta G^\circ_{1-3}$ Kcal/mole
39	Y^{3+}	11.62±0.02[a]	9.16±0.01	6.74±0.03	20.78±0.03	27.52±0.04
57	La^{3+}	10.28±0.01	8.07±0.05	6.40±0.13	18.35±0.05	24.75±0.14
58	Ce^{3+}	10.59±0.02	8.58±0.06	6.90±0.15	19.17±0.06	26 07±0 16
59	Pr^{3+}	10.71±0.04	8.81±0.05	6.90±0.20	19.53±0 06	26.43±0 21
60	Nd^{3+}	10.86±0.04	8.97±0 05	7.00±0.17	19.83±0.07	26 83±0.19
62	Sm^{3+}	11 37±0.02	9.17±0.02	6 85±0.09	20.55±0.03	27 40±0 10
63	Eu^{3+}	11 50±0.07	9.29±0.01	6.96±0.04	20.79±0.07	27 75±0 08
64	Gd^{3+}	11 52±0.02	9.13±0.01	6.78±0.03	20.65±0 02	27 43±0 03
65	Tb^{3+}	11.67±0.02	9.27±0.01	6.87±0.02	20.94±0.02	27.80±0.03
66	Dy^{3+}	11.69±0 02	9.22±0.01	6.78±0.02	20.91±0.02	27.69±0.03
67	Ho^{3+}	11.69±0.02	9.24±0.01	6.83±0.10	20.93±0.03	27.76±0.10
68	Er^{3+}	11.72±0.02	9.26±0.01	6.83±0.02	20.98±0.02	27.81±0.03
69	Tm^{3+}	11.76±0.02	9.33±0.01	6.92±0.03	21.09±0.02	28.01±0.03
70	Yb^{3+}	11.82±0.02	9.40±0.01	6.91±0.01	21.22±0.02	28.13±0.02
71	Lu^{3+}	11.79±0.03	9.44±0.01	7.04±0.02	21.23±0.03	28.28±0.03

[a] Standard deviation of value.

TABLE 3—ENTHALPY OF FORMATION OF Ln^{3+}-1-METHOXY-2,4-PENTANEDIONE CHELATES IN 50.0 (v/v) % DIOXANE-WATER MEDIUM AT 30.00±0.01°

Z	M^{3+}	ΔH°_1 Kcal/mole	ΔH°_2 Kcal/mole	ΔH°_3 Kcal/mole	$\Delta H^\circ_{1,2}$ Kcal/mole	$\Delta H^\circ_{1,3}$ Kcal/mole
39	Y^{3+}	2.03±0.6[a]	−2.89±1.0	−0.46±0.8	0.86±1.2	−1.32±1.4
57	La^{3+}	2.25±0.2	−1.85∓0 4	−3 39±1.1	0.40±0.4	−3.00±1.2
58	Ce^{3+}	2.31±0.1	−3.36±0.7	−1.23±2 0	−1 05±0.7	−2.28±2.1
59	Pr^{3+}	2.38±0.1	−3.66±0.5	−1.34±1.3	−1.28±0.5	−2.62±1.4
60	Nd^{3+}	1.69±0 2	−2.73±0.5	−2.12±1.3	−1.04±0 6	−3.16±1.4
62	Sm^{3+}	0.58±0.1	−0.76±0.5	−4.14±1.5	−0.19±0.5	−4.33±1.5
63	Eu^{3+}	2.61±0.3	−2.82±0 5	−2.51±0 7	−0.21±0.6	−2.72±1.0
64	Gd^{3+}	2 75±0.4	−0.35±0 7	−4 00±0.6	2.40±0.8	−1.61±1.0
65	Tb^{3+}	0.93±0.5	−1.78±1.0	0.58±0.8	−0 84±1.1	−1.42±1.4
66	Dy^{3+}	2.39±0.3	−2.79±0.6	−1.39±0.5	0.40±0.7	−1.79±0.9
67	Ho^{3+}	2 60±0 2	−3 26±0.3	−0 62±0 3	−0.66±0 3	−1.28±0.4
68	Er^{3+}	−0.69±0.2	3.77±0.6	−6.07±1.0	3.08±0.6	−2.99±1.2
69	Tm^{3+}	−0.14±0.5	1.18±0.9	−1.64±0.7	1.04±1.0	−0.60±1.2
70	Yb^{3+}	1.42±0.5	0.10±0.9	−0.92±0 8	1.52±1.0	0.60±1.3
71	Lu^{3+}	−0.99±0.4	2.63±0 8	−2 32±0.7	1.64±0.9	−0.68±1.1

[a] Standard deviation of the value.

TABLE 4—ENTROPY OF FORMATION OF Ln^{3+}-1-METHOXY-2,4-PENTANEDIONE CHELATES IN 50.0 (v/v) % DIOXANE-WATER MEDIUM AT 30 00±0 01°

Z	M^{3+}	ΔS°_1 E. U	ΔS°_2 E. U.	ΔS°_3 E. U.	$\Delta S^\circ_{1,2}$ E. U.	$\Delta S^\circ_{1,3}$ E. U.
39	Y^{3+}	45 0±1 8[a]	20.7±3.3	20.7±2 6	65.7±3.8	86.4±4.6
57	La^{3+}	41.3±0.5	20.5±1.3	9.9±3.6	61.8±1.4	71.8±3.9
58	Ce^{3+}	42 6±0.4	17.2±2 1	18.7±6.1	59 8±2.1	78 5±6.5
59	Pr^{3+}	43 2±0 3	17.0±1.6	18.4±4.2	60 2±1.6	78.5±4.5
60	Nd^{3+}	41 4±0.7	20.6±1.7	16 1±4.2	62 0±1.8	78.1±4.6
62	Sm^{3+}	39.4±0.4	27.7±1.6	8 9±4.7	67 2±1.6	76.1±4.9
63	Eu^{3+}	46.6±0.9	21.3±1.9	14.7±2.2	67.9±2.1	82.5±3.1
64	Gd^{3+}	47.1±1.2	28.9±2.2	9.2±2 0	76.0±2.5	85.2±3.1
65	Tb^{3+}	41.6±1 7	24.7±3.2	20.7±2.5	66.3±3 6	87.0±4.4
66	Dy^{3+}	46 4±1.0	21.2±1.9	17.8±1.6	67.7±2.2	85.4±2.7
67	Ho^{3+}	47 1±0.5	19.7±0 9	20 5±0.9	66 9±1.1	87.3±1.4
68	Er^{3+}	36.4±0 7	43.0±1 8	2.5±3 3	79.4±1 9	81.9±3.8
69	Tm^{3+}	38.3±1 6	34.7±2 8	17.4±2.2	73.0±3.2	90.4±3.9
70	Yb^{3+}	43.7±1 5	31.3±2.8	19.8±2.5	75.0±3.2	94.8±4.1
71	Lu^{3+}	35.6±1.4	39 8±2 5	15 6±2 3	75 5±2.8	91.0±2.8

[a] Standard deviation of the value

Changes in the enthalpy and entropy of complex formation when plotted as a function of atomic number of tervalent lanthanide show a complex pattern, Fig. 2-4. The values for ΔH°_1 and ΔH°_2 decrease from Z=57 to 71 with notable breaks (minima) at Z=62−63, 64−65 and 68. The values of ΔH°_3 show, in contrast, a general increase from Z=57−71 with notable deviations at Z=63 (minimum) and 68 (maximum). The significant common feature is the direct relationship between the change in enthalpy and change in entropy. Both tend to show parallel increases in the variations with atomic number of the lanthanide metal ion.

The latter observation is worth stressing that an interpretation may be made in terms of the structure of the reacting species.

Discussion

This study was the first application of a continuous addition technique to a lanthanide-ligand system in a mixed solvent system which permitted truly thermodynamic constants to be obtained. Although incremental addition techniques may be more accurate, the continuous addition technique affords the advantages of rapidity and convenience. The chief problems, apart from experimental design, were the computations of species distributions as a function of addition of titrant. These were solved through the aid of appropriate programs for high-speed computers[8].

The data presented here support an interpretation of an expanded solvation sphere through the lanthanide series. The nature of the solvation sphere is open to interpretation, owing to the mixed solvent system used, but it appears that dioxane has a greater role in the deaggregation of water molecules than as an actual solvation participant. Data obtained in this study, together with the data obtained by Kido and Fernelius[7], amply support this view.

Anomalies in chelating tendencies at gadolinium and at erbium are still difficult to explain in an unambiguous manner. The anomalies may constitute a type of cross-over point at which the variations in solvent-metal and ligand-metal interactions result in a break in the ligand metal bonding process through the series. For example, if the β-diketone changes from terdentate to bidentate near gadolinium and erbium in the lanthanide series, then the observed entropy anomaly would be understandable; a
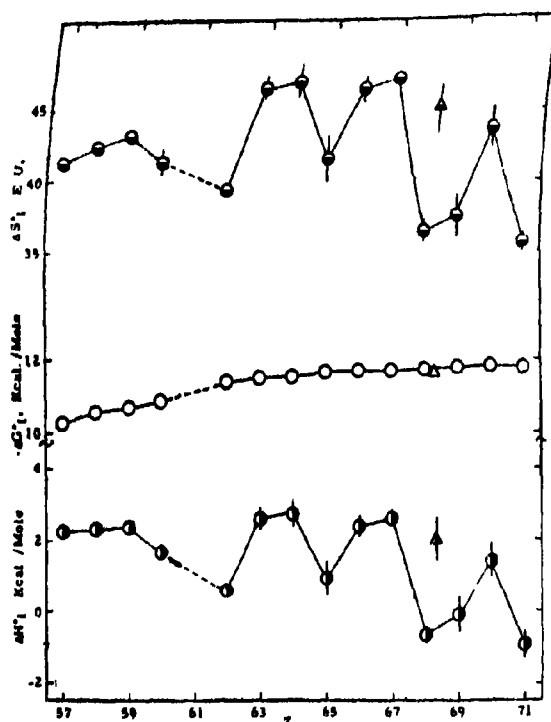
Fig 2. Thermodynamic parameters, ΔG°_1, O, Kcal/mole, ΔH°_1, O, Kcal mole; and ΔS°_1, O, E. U, as a function of atomic number, Z for the first step of chelate formation for the lanthanide-1-methoxy-2,4 pentanedione system. If the standard deviation of the value exceeds the representative circle, it is indicated by a vertical bar. The position of yttrium in the series is represented by the symbol Δ

Fig. 3. Thermodynamic parameters, $\Delta G^\circ_{1,2}$, O, Kcal/mole; $\Delta H^\circ_{1,2}$, O, Kcal/mole; and $\Delta S^\circ_{1,2}$, O, E. U., as a function of atomic number, Z, for the first and second steps of chelate formation for the lanthanide-1-methoxy-2, 4-pentanedione system. If the standard deviation of the value exceeds the size of the representative circle, it is indicated by a vertical bar. The position of yttrium in the series is represented by the symbol Δ.

decrease in the entropy of chelation should result in a decrease in the enthalpy of chelation in as much as the bond not formed would involve the other oxygen atom of the ligand. There is evidence for this type of non-involvement in the complexes of lanthanides with pyramidone[12]. With this system, chelation involves an amine nitrogen atom plus one ring nitrogen atom both, not the other. The second ring nitrogen atom presumably does not bond for steric reasons; the effect of solvent system was implied though not delineated[12].

Possibly, higher coordination or solvation must be invoked to account for the small differences in the chelating tendencies of 1-methoxy-2,4-pentanedionate with tervalent lanthanides. If a solvent species is not held tenaciously in the second or third solvation spheres, the removal of this species should have less impact on macrochemical observations (e.g., formation constant, change in entropy, change in enthalpy) than the removal of the same solvent species from the first coordination sphere. The logic of this statement derives from the fact that ΔG°, ΔS° and ΔH° are state functions that are subject to time averaging if a rapid exchange in the initial and final states exists. A more labile species possesses more energy (S° initial) and is held less tenaciously (less H° initial); thus the overall-state functions ΔG°, ΔS° and ΔH° of chelation are less affected by species in the second and third solvation spheres than those in the first sphere.

The results of this study, more specifically, are consistent with two processes (1) a decrease in the first solvation sphere around gadolinium and (2) an increased solvation of other lanthanide ions The former process has been proposed and supported by Hoard[13] and by Grenthe[14]; the second by Padova[15]. The hypothesis that the coordination sphere is drastically disrupted by the first chelation process is supported by large values of ΔS_1 and the large positive values of ΔH_1.

The final delineation of the solution structure of lanthanide ions may be completed through the use of several methods. Investigation of activity data for these ions in various solvents offers promise[16]. Another approach may be the use of radiation diffraction techniques in very concentrated solutions[17]. In any event, equilibrium data will contribute to the ultimate solution of the gadolinium break by pointing the way to more structurally oriented techniques. The fact that the observations made in this study support prevalent theories of coordination number change suggests that the true
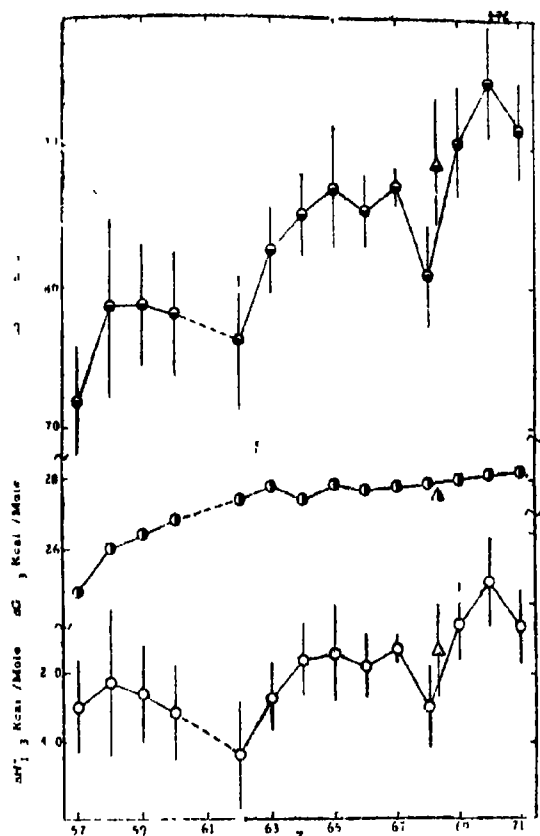
Fig. 4. Thermodynamic parameters, $\Delta G^{\circ}_{1,3}$, ◐, Kcal/mole ; $\Delta H^{\circ}_{1,3}$, ○, Kcal/mole, $\Delta S_{1,3}$, ◒, E. U., as a function of atomic number, Z, for the first, second and third steps of chelate formation for the lanthanide-1-methoxy-2,4 pentanedione system. If the standard deviation of the value exceeds the size of the representative circle, it is indicated by a vertical bar. The position of yttrium in the series is represented by the symbol Δ.

interpretation is probably a synthesis of the two. The method used in this study is shown to be valid for a solvent system other than water, and for this the thermodynamic properties of the lanthanides may be investigated in a variety of closely related solvent systems with varying dielectric constants This approach should permit the ultimate evaluation of the activity data needed to infer structural characteristics.

Ultimately, the problem of the gadolinium break and other apparent anomalies may be more a problem of the structure of water than a problem of the exact coordination tendencies of the lanthanides. This possibility awaits the investigations of systems that involve much less hydrogen bonding and that are less polar than water. The present study indicated the direction and some of the methods that these studies may take.

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Coordination of Al(III), Be(II) and Cu(II) Ions with 1,7-Dihydroxy-4-sulfo-2-naphthoic and 3,5-Dihydroxy-7-sulfo-2-naphthoic Acids in Aqueous Sodium Perchlorate Medium

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The aluminium(III), beryllium(II) and copper(II) complex formation of sodium 1,7-dihydroxy-4-sulfonato-2-naphthoic and sodium 3,5-dihydroxy-7-sulfonato-2-naphthoic acids, $Na^+H_3L^-$, has been studied in aqueous solution at ionic strength 0.5 ($NaClO_4$ as main electrolyte) and $25.0 \pm 0.1°$ by means of potentiometric *p*H titrations. The protonation of the ligand anions has been investigated by standard spectrophotometric and potentiometric methods under the same conditions.

In the metal-ligand equilibrium systems, the experimental data can be explained with the formation of the complexes MHL^-, ML^{2-}, $MH_2L_2^{4-}$, MHL_2^{5-} and ML_2^{6-} (M = Cu or Be), and AlHL, AlL^-, $AlHL_2^{4-}$, AlL_2^{5-} and AlL_3^{9-} when an excess of the ligand is present and *p*H <9. Polynuclear complex compounds were not found in detectable amounts in potentiometric titrations. However, this might be only due to the experimental conditions, since accurate potential readings were available only with an excess of the ligand in the solutions to be titrated.

POTENTIOMETRIC and spectrophotometric studies on the complexes formed between beryllium(II), copper(II) and aluminium(III) and a number of aromatic sulfo-substituted *o*-hydroxycarboxylic acids have been reported in our previous papers[1-7]. All the previous ligands have been mono- or disulfonic acid derivatives of salicylic, 1-hydroxy-2-naphthoic or 3-hydroxy-2-naphthoic acids, thus containing one hydroxyl group and one carboxyl group in *ortho*-positions to each other, and one or two sulfonato groups. 1,7-Dihydroxy-4-sulfo-2-naphthoic and 3,5-dihydroxy-7-sulfo-2-naphthoic acids are new reagents for investigation of metal complex formation and the number of hydroxyl groups is the main difference between these and the compounds studied earlier. The present investigation was undertaken to determine the composition and stability of the species formed in the equilibrium system : H^+-ligand, Be^{2+}-ligand, Cu^{2+}-ligand and Al^{3+}-ligand (where ligand is either 1,7-dihydroxy-4-sulfonato-2-naphthoic acid or 3,5-dihydroxy-7-sulfonato-2-naphthoic acid anion). A comparison of the results obtained with 1-hydroxy-4-sulfo-2-naphthoic, 1-hydroxy-7-sulfo-2-naphthoic, 1-hydroxy-4, 7-disulfo-2-naphthoic, 3-hydroxy-4-sulfo-2-naphthoic, 3-hydroxy-5-sulfo-2-naphthoic, 3-hydroxy-7-sulfo-2-naphthoic and 3-hydroxy-5,7-disulfo-2-naphthoic acids permits a discussion of the effects of the "lone" hydroxyl group (the hydroxyl group without neighbouring substituents) on the protonation and metal complex formation of the salicylic-type ligands of the naphthalene series. The stability constants of Be^{2+}, Cu^{2+} and Al^{3+} complexes with 1,7-dihydroxy-4-sulfo-2-naphthoic aci[d] have been reported in an earlier paper[8].

The experimental methods used in this invest[i]gation were the same as described in the earli[er] studies, i.e. standard potentiometric and spectr[o]photometric methods. All experiments were pe[r]formed in a medium of ionic strength 0.5 *M*, wit[h] sodium perchlorate as the neutral salt. The tempe[rature] was $25.0 \pm 0.1°$.

Notations :

1,7-Dihydroxy-4-sulfonato-2-naphthoic acid an[d] 3,5-dihydroxy-7-sulfonato-2-naphthoic acid anion[s] $[C_{10}H_4SO_3(OH)_2COOH]^-$, are written as H_3L^-. C_M, C_H and C_L denote the total concentrations o[f] metal, free and dissociable hydrogen ions, and ligan[d] anion, respectively. [M], [H^+] and [L] denote th[e] concentrations of free metal ion, hydrogen ion an[d] ligand anion respectively.

$\beta_{q,p,r}$ is the overall stability constant for th[e] complex $M_qH_pL_r$, defined as

$$\beta_{q,p,r} = [M_qH_pL_r]/[M]^q[H]^p[L]^r \quad \ldots (1)$$

where $q \geq 0$, $p \geq 0$, $r \geq 0$, and $q+p+r \geq 2$.

$$\bar{n}_H = (C_H - [H^+] + [OH^-])/C_L \quad \ldots (2)$$

$$\bar{n} = (C_L - \sum_{j=0}^{3} [H_jL])/C_M \quad \ldots (3)$$

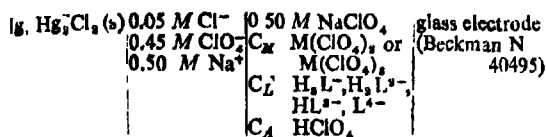
$\bar{n}_H$ = the mean number of hydrogen ions bound pe[r] ligand anion, and

$\bar{n}$ = the mean number of ligand anions bound pe[r] metal ion.

Experimental

Reagents : Sodium 1,7-dihydroxy-4-sulfonato-2-naphthoic and sodium 3,5-dihydroxy-7-sulfonato-2-naphthoic acids were prepared on alkali fusion from 1-hydroxy-4,7-disulfo-2-naphthoic acid and -hydroxy-5,7-disulfo-2-naphthoic acid, respectively The purity of the compounds was checked by ^{1}H and ^{13}C nmr spectrometry.

Potentiometric measurements : The emf (E) of a galvanic cell of the following type was measured :

Hg, Hg_2Cl_2(s) | 0.05 M Cl^-, 0.45 M ClO_4^-, 0.50 M Na^+ | 0 50 M $NaClO_4$, C_M $M(ClO_4)_2$ or $M(ClO_4)_3$, C_L H_4L^-, H_2L^{2-}, HL^{3-}, L^{4-}, C_A $HClO_4$ | glass electrode (Beckman N 40495)

The system was calibrated before each titration by measuring the emf (E_R) when the titration vessel contained a solution of known free hydrogen ion concentration, $[H^+]_R$. The unknown hydrogen ion concentration, $[H^+]$, was then calculated from the equation :

$$-2.303\,RT/F \log([H^+]/[H^+]_R) = (E_R - E_j') - (E - E_j'') \quad .. \quad (4)$$

where $R=8.314$ JK^{-1}mol^{-1}, $T=298.15$ K and $F=96\,487$ C mol^{-1}. E_j' and E_j'' are the liquid junction potentials. The liquid junction potentials depend mainly on the free hydrogen ion concentration in the solutions, and E_j is then a linear function of $[H^+]$($E_j([H^+]) = j([H^+])$, where j is a constant).

The potentiometric measurements were carried out with a Radiometer digital titration system DTS 633, consisting of an autoburette ABU 13 or 80, a pH meter, PHM 64, and a digital titrator, TTT 61, with an equal increment accessory constructed in this laboratory[9].

The protonation constants of the ligand anions were determined in solutions without any metal present. In these measurements C_L was kept constant and C_H was varied by adding NaOH or $HClO_4$ to the solution with different $C_L : C_H$ ratios. The experimental data for evaluating the protonation constants consist of seven different emf titrations for each ligand acid, where C_L and -log $[H^+]$ varied between 0.001 and 0.03 M, and 2.3 and 12, respectively.

The stabilities of the beryllium(II), aluminium(III) and copper(II) complexes of 1,7-dihydroxy-4-sulfo-2-naphthoic and 3,5-dihydroxy-7-sulfo-2-naphthoic acids were determined by measuring the emf values in galvanic cells of the kind described above During the titrations the ratio $C_L : C_M$ was kept constant and C_H was varied by adding NaOH. The concentrations C_M and C_L in the starting solutions and the -log $[H^+]$ ranges for the Be^{2+}, Al^{3+} and Cu^{2+} systems with 3,5-dihydroxy-7-sulfo-2-naphthoic acid are given in Table 1.

Spectrophotometric measurements : A Pye Unicam SP 8—100 UV-vis spectrophotometer, equipped with a 10 mm autocell and a superimpose accessory was used for the purpose. The absorbance readings were taken in the wavelength range 300—420 nm with an interval of 5 nm. C_L was varied in these measurements between 0.00005 and 0.0003 M. In evaluating the protonation constants of the ligand anion, altogether 36 test solutions were prepared with varying pH values (2 < -log $[H^+]$ < 13.5) for each H^+-ligand system.

TABLE 1—NUMBER OF POTENTIAL READINGS, INITIAL CONCENTRATIONS, C_M AND C_L, AND THE −LOG $[H^+]$ RANGES FOR THE TITRATIONS CARRIED OUT FOR EVALUATING THE STABILITY CONSTANTS OF THE BERYLLIUM(II), ALUMINIUM(III) AND COPPER(II) 3,5 DIHYDROXY-7-SULFONATO-2-NAPHTHOIC ACID COMPLEXES

Expt.	No of readings	Metal	C_M/M	C_L/M	log $[H^+]$ range
1	47	Be	0.00096	0.00315	3.21–9.49
2	55	,,	0.00096	0.00323	3.20–8.26
3	54	,,	0.00096	0.00545	3.20–8.06
4	38	,,	0.00192	0.00323	3.16–6.34
5	44	,,	0.00192	0.00538	3.11–7.79
6	34	,,	0.00384	0.00539	3.07–6.09
7	58	,,	0.00384	0.02150	3.09–8.21
8	36	Al	0.00097	0.00330	3.10–6.03
9	44	,,	0.00097	0.00550	3.10–8.42
10	57	,,	0.00097	0.00770	3.13–8.13
11	47	,,	0.00194	0.00704	3.07–8.07
12	53	,,	0.00194	0.01408	3.07–8.21
13	58	,,	0.00194	0.02816	3.04–8.11
14	57	,,	0.00388	0.02820	3.00–8.07
15	33	Cu	0.00099	0.00218	3.38–9.98
16	41	,,	0.00099	0.00327	3.40–9.08
17	45	,,	0.00099	0.00545	3.44–8.25
18	51	,,	0.00149	0.00545	3.41–8.15
19	55	,,	0.00200	0.00545	3.36–8.91
20	53	,,	0.00399	0.01090	3.32–8.75
21	55	,,	0.00399	0.02180	3.00–8.80

Calculations : The equilibrium constants were calculated as overall stability constants (Equation 1) with the programme SCOGS[10] from the potentiometric data and with the programme SQUAD[11] from the spectrophotometric (absorbance-pH) data on a Univac 1100/20 computer.

Results and Discussion

The proton-ligand systems : The search of the potentiometric data was initiated by drawing the

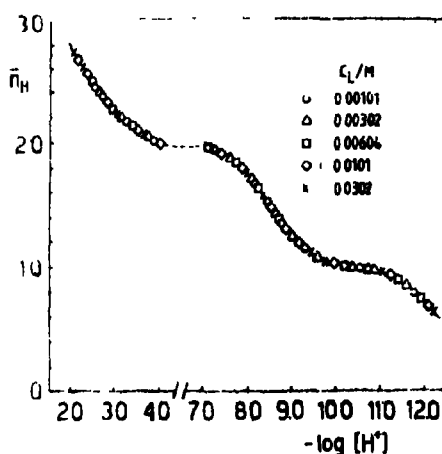



Fig. 1. Experimental (points) and calculated (solid line) $\bar{n}_H$ values vs −log $[H^+]$ for 3,5-dihydroxy-7-sulfo-2-naphthoic acid at $I = 0.5$ ($NaClO_4$) and $t = 25°$.

$\bar{n}_H$ vs (-log [H^+]) plots for both H_l^+-ligand systems (Fig. 1). It can be seen from the figure that the $\bar{n}_H$ (-log [H^+]) function is independent of C_L, which would indicate that only a series of monomeric H_iL species is formed. These plots further suggest that these species are H_3L^-, H_2L^{2-}, HL^{3-} and L^{4-}, because the $\bar{n}_H$ values are all between 2.4 and 0.9 and 2.8 and 0.7, respectively, for 1,7-dihydroxy-4-sulfo-2-naphthoic acid and 3,5-dihydroxy-7-sulfo-2-naphthoic acid. A least-squares refinement of the potentiometric data gave the values of the protonation constants as shown in Table 2.

Fig. 2 and 3 show the uv-vis absorption spectra of 1,7-dihydroxy-4-sulfo-2-naphthoic and 3,5-dihydroxy-7-sulfo-2-naphthoic acids at various pH values between 2 and 13. As can be seen, there are three distinct pH regions displaying different patterns of change in the absorption spectra of the ligand acids : (1) about 2 < pH < 5, (2) 5 < pH < 10 and pH > 10. In both systems isosbestic points appear at distinct pH regions, which also suggest that three different protonation reactions take place in the pH range studied. Spectral data for the ligand anions studied are compiled in Table 3, and the protonation constants, obtained spectrophotometrically in Table 2.

TABLE 2—THE PROTONATION CONSTANTS OF 3,5-DIHYDROXY-7-SULFO-2-NAPHTHOIC (1) AND 1,7-DIHYDROXY-4-SULFO-2-NAPHTHOIC (2) ACIDS AT I = 0.5 ($NaClO_4$) AND 25°. THE QUOTED ERRORS ARE THREE TIMES THE STANDARD DEVIATIONS $k_{0,2,1} = K(HL^{3-} + H^+ = H_2L^{2-})$ AND $k_{0,3,1} = K(H_2L^{2-} + H^+ = H_3L^-)$, gl = POTENTIOMETRIC METHOD AND sp = SPECTROPHOTOMETRIC METHOD

Ligand/method	log $\beta_{0,1,1}$	log $\beta_{0,2,1}$	log $\beta_{0,3,1}$	log $k_{0,2,1}$	log $k_{0,3,1}$	Refs.
(1)/gl	12.355±0.015	20 809±0 018	23.314±0.003	8.45	2 50	This work
(1)/sp	12.374±0.021	20.745±0.024	23.268±0.012	8.37	2.52	,,
(2)/gl	11.93 ±0.10	20 806±0 010	23.469±0.007	8 88	2.66	8
(2)/sp	12 254±0.050	21.064±0 010	23.748±0.006	8.81	2.68	8

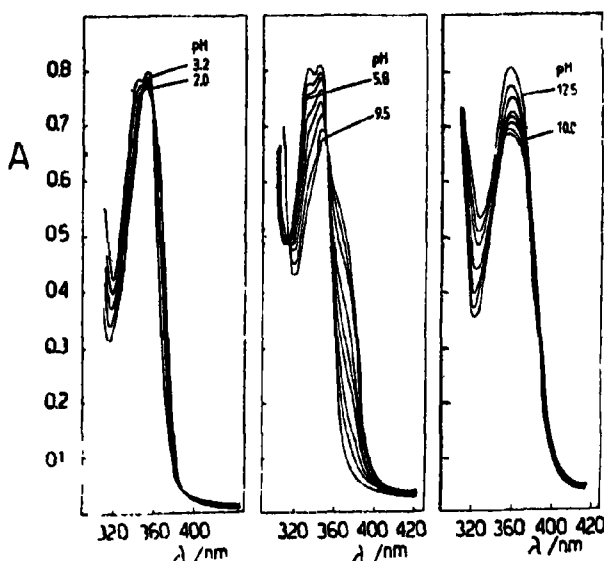



Fig. 2. UV-vis absorption spectra of 1,7-dihydroxy-4-sulfo-2-naphthoic acid at various pH values between 2 and 13 (C_L = 0.0002 M) at I = 0.5 ($NaClO_4$) and t = 25°.

Comparison of the protonation constants obtained potentiometrically and spectrophotometrically shows that the values of each constant for 3,5-dihydroxy-7-sulfo-2-naphthoic acid and the values of the second and third protonation constants for 1,7-dihydroxy-4-sulfo-2-naphthoic acid are in fair agreement with each other, whereas the log $\beta_{0,1,1}$ value for 1,7-dihydroxy-4-sulfo-2-naphthoic acid evaluated potentiometrically is about 0.3 log units lower than that determined spectrophotometrically. Because the first protonation reaction takes place in very alkaline solutions, the spectrophotometric method (when buffer solutions are used) is more reliable than the potentiometric method

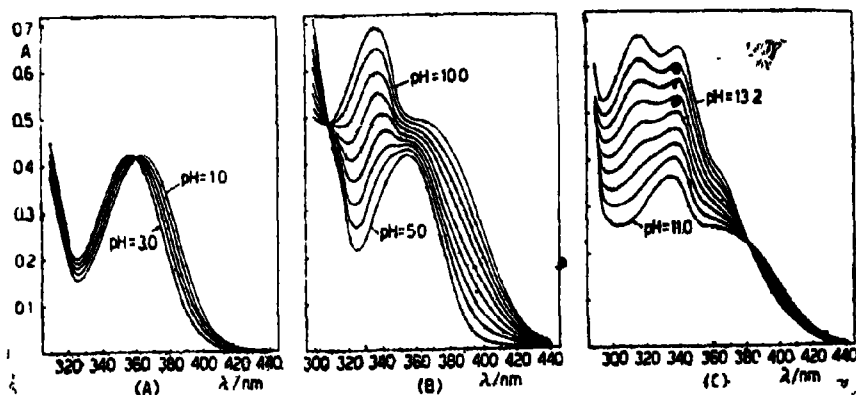



Fig. 3. UV-vis absorption spectra of 3,5-dihydroxy-7-sulfo-2-naphthoic acid at various pH values between 1 and 13.2 (A and B: C_L = 0.000226 M and C: C_L = 0.000113 M) at I = 0.5 ($NaClO_4$) and t = 25°.

TABLE 3—THE SPECTRAL DATA FOR 1,7-DIHYDROXY-4-SULFO-2-NAPHTHOIC AND 3,5-DIHYDROXY-7-SULFO-2-NAPHTHOIC ACIDS IN AN AQUEOUS SOLUTION AT 25°

Species	λ_{max}/nm	ϵ^{max}/cm^{-1}M^{-1}	Isosbestic points/nm
1,7-Dihydroxy-4-sulfo-2-naphthoic acid			
H_3L^-	358.5	3 840	} 358 and 392
H_2L^{2-}	336.5	4 000	
	346.5	4 040	} 314 and 354
HL^{3-}	360 0	3 400	
L^{4-}	359.0	4 000	
3,5-Dihydroxy-7-sulfo-2-naphthoic acid			
H_3L^-	364.5	1 860	
H_2L^{2-}	355 0	1 850	} 360.0
HL^{3-}	336.0	3 090	} 309 5
L^{4-}	314 0	5 800	} 381.0
	334.0	5 700	

(when the glass electrode is used). Hence the value obtained spectrophotometrically for log $\beta_{0,1,1}$ for 1,7-dihydroxy-4-sulfo-2-naphthoic acid was used in the calculations of the stability constants of the metal complexes.

The present ligands seem to be weaker as acids with respect to the neighbouring carboxyl and hydroxyl groups than the various mono- and disulfonato derivatives of 1- and 3-hydroxy-2-naphthoic acids studied earlier when the difference between the ionic strengths in the determinations has been taken into account[1-9]. Further, it can be noted that the protonation constants of the hydroxyl groups at carbons C-7 and C-4 are about the same as those of 1- and 2-naphtholsulfonates[12]. It is also worth adding that none of the studied sulfonated hydroxycarboxylic acids, including the present dihydroxy derivatives, dimerizes within the available concentration limits.

3,5-Dihydroxy-7-sulfo-2-naphthoic acid is a stronger acid than 1,7-dihydroxy-4-sulfo-2-naphthoic acid with respect to the "lonesome" hydroxyl group as well as the carboxyl group, whereas the acidity of the other hydroxyl group seems to be the reverse.

The metal-ligand systems: The search for the complex species in the different metal-ligand systems was begun as usual by drawing the Bjerrum plots, $\bar{n}$=f(-log[L]), for each system. As can be seen from Fig 4, $\bar{n}$ is not only a function of -log[L] for the copper-ligand equilibrium system, but depends

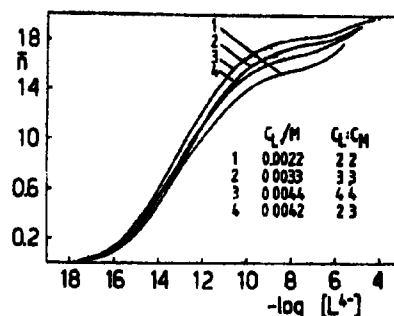



Fig. 4. Part of the experimental data presented as $\bar{n}$(−log [L]) curves for copper(II)-1,7-dihydroxy-4-sulfo-2-naphthoic acid equilibrium system.

as well on C_L. Thus, the formation of the complexes MH_pL_r (p≠0) must be taken into consideration. The same observation was made for the other equilibrium systems. The highest experimental $\bar{n}$ values for the beryllium or copper, and aluminium systems were under 2 and 3, respectively, indicating that complexes with at least two ligands per beryllium or copper ion and three ligands per aluminium ion must be formed. Several sets of constants of different MH_pL_r complexes were calculated for each metal-ligand equilibrium system. The reliability of the equilibrium constants obtained in these calculations was checked through comparison of the experimental and calculated $\bar{n}$ values. The best explanations for the potentiometric data were the sets of the complexes MHL^-, ML^{2-}, $MH_2L_2^{4-}$, MHL_2^{5-} and ML_2^{6-} (M=Be or Cu) and AlHL, AlL^-, $AlHL_2^{4-}$, AlL_2^{5-} and AlL_3^{9-} with the stability constants given in Table 4. It is reasonable to consider that the protons in the "acidic" complexes are those of the hydroxyl group at carbon C−7 or C−4, and that the ML_r species are formed either (a) via the dissociation of these protons or (b) via the direct reduction between metal and L^{4-} anions. Polynuclear complex compounds were not found in detectable amounts in potentiometric titrations. However, this might only be due to the experimental conditions, since accurate potential readings were available only with an excess of the ligand in the solutions to be titrated. Spectrophotometric

TABLE 4—THE STABILITY CONSTANTS FOR THE DIFFERENT METAL-3,5-DIHYDROXY-7-SULFO-2-NAPHTHOIC ACID AND METAL-1,7-DIHYDROXY-4-SULFO-2-NAPHTHOIC ACID EQUILIBRIUM SYSTEMS AT I=0.5 ($NaClO_4$) AND 25°

q, p, r	log $\beta_{Al_qH_pL_r}$	log $\beta_{Be_qH_pL_r}$	log $\beta_{Cu_qH_pL_r}$	Refs
Metal-3,5-Dihydroxy-4-sulfo-2-naphthoic acid system				
1,1,1	20 651±0.026	20.004±0.015	17.805±0 018	This work
1,0,1	16 001±0 025	13.64 ±0.10	10.205±0.025	"
1,2,2	–	37 996±0.036	33.162±0 046	"
1,1,2	32.443±0.042	29.848±0 036	24 60 ±0 05	"
1,0,2	24 089±0.048	20.789±0.046	15.885±0.036	"
1,0,3	30.849±0 048	–	–	"
Metal-1,7-Dihydroxy-4-sulfo-2-naphthoic acid system				
1,1,1	20.001±0.022	20.327±0.015	18.576±0.030	8
1,0,1	14.952±0.030	14.43 ±0.05	11.79 ±0.06	"
1,2,2	–	38.762±0.025	35.56 ±0.05	"
1,1,2	30.80 ±0.08	30.11 ±0.05	27.06 ±0.05	"
1,0,2	22.14 ±0.09	20.854±0.030	17.418±0.040	"
1,0,3	28.21 ±0.08	–	–	"

measurements confirmed the polymerization in acidic metal-ligand solutions where there was a large excess of metal ion with respect to the ligand (Fig. 5).

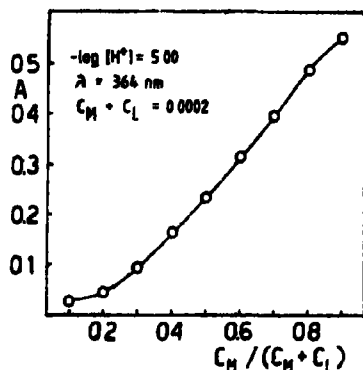



Fig. 5. Absorbance plot obtained by the continuous variation method for beryllium(II)-1,7-dihydroxy-4-sulfo-2-naphthoic acid system.

The stability of the present metal complexes follows the general order obtained many times earlier with related chelation agents containing oxygen-oxygen donor atoms, viz, $AlL_n > BeL_n > CuL_n$.

The beryllium and copper 1,7-dihydroxy-4-sulfonato-2-naphthoic acid complexes are more stable than the corresponding 3,5-dihydroxy-7-sulfonato-2-naphthoic acid complexes. In the case of the aluminium complexes the mutual stability order is reverse.

The present dihydroxy-2-naphthoic acid sulfonates form more stable 1 : 1 complexes than the different mono- and disulfonato derivatives of 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acids. On the other hand, the addition of a second ligand molecule to the ML complexes is significantly more difficult when the sulfonato group at the carbon C-5 of 3-hydroxy- ,7-disulfonato-2-naphthoic acid or at carbon C-7 of 1-hydroxy-4,7-disulfonato-2-naphthoic acid is replaced with the hydroxyl group (the log k_1/k_2 values for the 1,7-dihydroxy-4-sulfonato-2-naphthoic acid and 3,5-dihydroxy-7-sulfonatonaphthoic acid complexes are about twice those for the 1-hydroxy-4,7-disulfonato-2-naphthoic acid and 3-hydroxy-5,7-disulfonato-2-naphthoic acid complexes).

TABLE 5—THE PROTONATION CONSTANTS OF ML AND ML_2 (CHARGES ARE OMITTED) COMPLEXES OF 3,5-DIHYDROXY-7-SULFO-2-NAPHTHOIC AND (1) AND 1,7-DIHYDROXY-4-SULFO-2-NAPHTHOIC ACID (2) AT I = 0.5 ($NaClO_4$) AND 25°. $K^H_{1,1,1} = K(ML+H = MHL)$, $K^H_{1,1,2} = K(ML_2+H = MHL_2)$ AND $K^H_{1,2,2} = K(MHL_2+H = MH_2L_2)$

Metal	Ligand	log $K^H_{1,1,1}$	log $K^H_{1,1,2}$	log $K^H_{1,2,2}$	Refs.
Al	(1)	4.65	8.35	–	This work
Be	,,	6.36	9.06	8.15	,,
Cu	,,	7.60	8.72	8.56	,,
Al	(2)	5.05	8.66	–	8
Be	,,	5.90	9.26	8 65	,,
Cu	,,	6.79	9.64	8.50	,,

Table 5 shows the protonation constants of the 1 : 1 and 1 : 2 complexes. The following conclusions can be drawn on the basis of these constants: (a) the acidity of the protons in the MH_pL_r complexes increases with the increasing stability of the

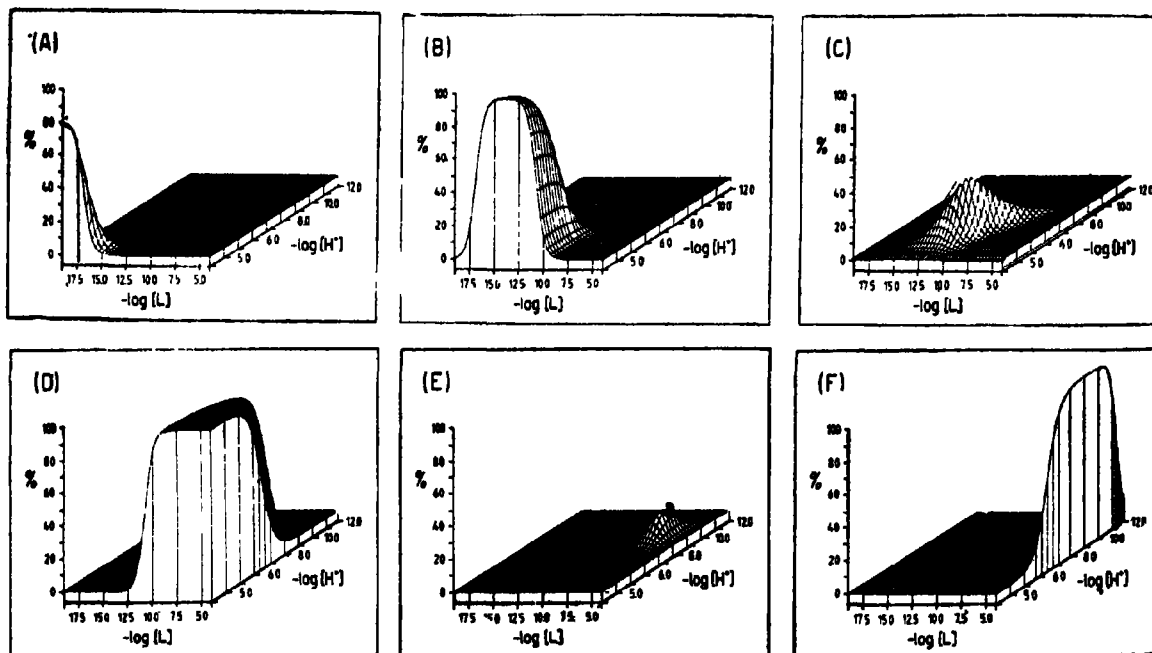



Fig. 6. Three-dimensional representation of the formation of the different aluminium species: (A) Al^{3+}, (B) AlHL, (C) AlL^-, (D) $AlHL_2^{4-}$, (E) AlL_2^{5-} and (F) AlL_3^{8-} with 1,7-dihydroxy-4-sulfo-2-naphthoic acid.

ML_r complexes, (b) the acidity of the hydroxyl group at carbon C-7 is significantly higher in the 1 : 1 complexes than in the free ligand anion and (c) the protonation constants of the 1 : 2 complexes are, on an average, of the same value as the second protonation constant of the ligand anion.

The aluminium(III), beryllium(II) and copper(II) complex formation of 1,7-dihydroxy-4-sulfo-2-naphthoic and 3,5-dihydroxy-7-sulfo-2-naphthoic acids depend on the free hydrogen ion and ligand anion concentrations if there is an excess of the ligand acid present in the solutions. Thus, all the present equilibrium systems can be displayed as a function of $[H^+]$ and $[L^{4-}]$. Fig. 6 shows the formation of various aluminium species three-dimensionally for 1,7-dihydroxy-4-sulfo-2-naphthoic acid in the *p*H and -log [L] ranges studied and assuming that there is an excess of the ligand present. For the sake of clarity, the formation of each species is presented in a separate figure

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A New Parameter in Astatistical Stabilization of Ternary Complexes

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The formation constants of the complexes of the type [CuAL], where A = 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen) and L = tryptophan have been determined in aqueous medium and $\mu = 0.2$ *M* ($NaClO_4$) at 30°. The formation constant values have been determined by graphical method and further refined by using a computer program SCOGS The value of Δlog K, (log K^{MA}_{MAL} − log K^{M}_{ML}), is found to be positive in [CuAL] complexes even though L is coordinating through amino acid end just as glycine. The higher stabilization of the ternary complexes is mainly due to release of electron repulsion in the ternary complex. There is repulsion between Cu(II) $d\pi$ electrons and electrons delocalized over the indole ring in binary complex. In the ternary complex, due to M→bipy π interaction, electrons pass over the bipyridyl molecule and there is less amount of electron repulsion leading to positive Δlog K.

VARIOUS aspects of the ternary complexes involving aromatic tertiary amines and various N-N, N-O⁻ and O⁻O⁻ coordinating ligands are being studied in detail because of the similarity of the aromatic tertiary amines with imidazole, which occurs commonly in biological systems. These complexes[1-3] provide models for metalloenzymes. Such complexes are also of interest as they exhibit an astatistical[2,3] stabilization due to special role of the aromatic tertiary amines. In the complexes [MAL], where A is a tertiary amine like 2,2'-bipyridyl (bipy), it has been observed that the mixed ligand formation constant log K^{MA}_{MAL} is higher than that expected from statistical considerations[4]. This has been explained to be due to M→bipy π interaction[5,6]. Consequently, effective electronegativity of $[MA]^{2+}$ is almost the same as in $[M(H_2O)_6]^{2+}$ and hence log $K^{M}_{ML} \simeq$ log K^{M}_{MAL}.

It has been further observed that $[MA]^{2+}$ complexes discriminate between secondary ligand (L) with coordinating sites, N-N, N-O⁻ and O⁻O⁻ [5,7-10]. In case where secondary ligand is malonate[11] coordinating through two oxygen atom, Δlog K, (log K^{MA}_{MAL}-log K^{M}_{ML}), is positive. Sigel has attributed the greater stabilization of ternary complexes containing O⁻O⁻ to an increase in class A character of [M.bipy] In keeping with this concept we have extended an explanation in terms of electron repulsion[12-14]. In the formation of binary complexes, there is electron repulsion between the metal $d\pi$ electrons and the lone pair of electrons (if any) present on the σ bonding ligand L. However, in the ternary complexes, due to back donation of electrons through π bonding from the metal ion to the molecule A, the electron density on $[CuA]^{2+}$ is reduced. Therefore, the repulsion between the metal $d\pi$ electrons and the additional lone pair of electrons over the secondary ligand L is less in the ternary complexes. There is no extra lone pair of electrons present on σ bonding N atom and hence this effect is not felt in N-N coordinating ligands. In ligands coordinating through N-O⁻ there is lone pa electrons over the carboxylate O⁻. Due to th crease of the electron repulsion in the te complexes, Δlog K is much less negative in than in N-N coordinating ligands. In case of (coordinating ligand like malonate there are pairs of electrons over both carboxylate anions hence the effect is more pronounced leading to tive Δlog K in [CuAL].

It has been further observed that in case w O⁻O⁻ is an aromatic ligand like [Cu(bipy)(c Δ log K is more positive. This additional stabi tion has been explained by Sigel[15] in terms of i ligand π interaction between two ligands thro metal $d\pi$ orbitals. However, Sigel presumed this interaction is not significant. Our studies *the electronic spectra of the complexes also do indicate any significant inter-ligand π interacti Hence an attempt has been made to explain stabilization in the ternary complexes involv aromatic O⁻O⁻ also in terms of electron repulsi Since the Cu(II) electrons are in t_{2g} orbitals with symmetry, the repulsion with the electrons on t p_z orbital of the coordinated O⁻O⁻ (catechol) w be more in the binary complex. Hence, there wi be greater release of repulsion and stabilization (the ternary complexes wherein $d\pi$ electrons o Cu(II) pass over the bipyridyl molecule. Anothe important observation made by Sigel[16] and also b* us[17], is that electron withdrawing groups on L reduce the stability of ternary complexes while electron releasing groups on L increase the stability. This has also been explained[17] in terms of the proposed electron repulsion concept. The electron withdrawing groups lower the electron density on the ligand atom. Hence, the electron repulsion in the binary complex is less and corresponding release of electron repulsion in ternary complex and it's stabilization is less.

Normally, Δlog K is found to be positive only

in cases where L is O-O⁻ coordinating ligands. It has been observed by us[12] that $\Delta \log K$ is positive in case of [CuAL] complex where A=2(2′-pyridyl)-benzimidazole and L=glycine having N-O⁻ coordinating site. This was explained to be due to increased Cu→Aπ interaction due to pyridyl and benzene rings of 2(2′-pyridyl)benzimidazole. Further, it has been observed by us[18] that $\Delta \log K$ is positive in cases of [CuAL] complexes, where A=bipy or phen and L=phenylalanine, tyrosine or dopa, coordinating from N-O⁻ site as in the case of glycine. It has been shown that the aminocarboxylate end of phenylalanine, tyrosine or dopa coordinates with [CuA] and the phenyl, phenol or catechol part remains free and spreads over the [CuA] part. There may be an intermolecular stacking interaction between the tertiary amine and the aromatic ring of the secondary ligand as suggested by Sigel in case of [Cu(*o*-phen)(phenylacetate)] complexes[19]. However, construction of a model shows that the aromatic ring of the secondary ligand can spread only over the axial region of the Cu(II) and not beyond. The greater stability of these ternary complexes can be explained in terms of release of electron repulsion. There is repulsion in the binary complex between the Cu(II) electrons and π electrons of secondary ligand phenyl group which can come over the metal ion. But in the ternary complexes due to M→A π interaction, the electron density over Cu^{2+} ion is effectively reduced and hence repulsion is reduced leading to the formation of stable ternary complex. In order to confirm the observation further, in the present study mixed ligand complexes [CuA tryptophan], where A=bipy (A^1) or phen (A^2), have been studied.

Experimental

All reagents used were of A.R. grade. The proton-ligand and metal-ligand formation constants were determined in aqueous medium and μ=0.2 *M* ($NaClO_4$) at 30°. The values of $\bar{n}H$, K_1^H, K_2^H, $\bar{n}$, p^L, $\log K_1$ and $\log K_2$ were calculated by carrying out Irving-Rossotti titrations[20,21]. The formation constants of ternary complexes were determined by using a modified Irving-Rossotti titration technique[6]

All the formation constants were subjected to refinement by using the computer program SCOGS[22]. Details of consideration of various species and use of computer program is as described in our earlier work[12-14]. The refined constants are tabulated in Tables 1 and 2. It is observed that

TABLE 1—PROTONATION CONSTANTS AND METAL LIGAND STABILITY CONSTANT OF COPPER COMPLEXES IN AQUEOUS MEDIUM, I-0.2 MOLE dm^{-3} ($NaClO_4$) AT 30°

Ligands	Protonation constant		Metal-ligand binary constant	
	K_1^H	K_2^H	K_1	K_2
A^1	4.45±0.01	1.5±0.1	8.1 ±0.01	5.5 ±0.03
A^2	4.96±0.01	1.9±0.1	9.25±0.02	4.54±0.09
Tryptophan (L′)	9 06±0.03	2.6±0.04	8 19±0.09	6.79±0.07

TABLE 2—STABILITY CONSTANT OF TERNARY COMPLEX AND LOG K IN AQUEOUS MEDIUM, I-0 2 MOL dm^{-3} ($NaClO_4$) at 30°

	CuA^1L^1		CuA^2L^1	
	$\log K^{MA}_{MAL}$	$\Delta \log K$	$\log K^{MA}_{MAL}$	$\Delta \log K$
L^1	9.75±0.03	+1.56	9.32±0.03	+1.13

the major species are [CuA] and [CuAL] as shown in Fig. 1.
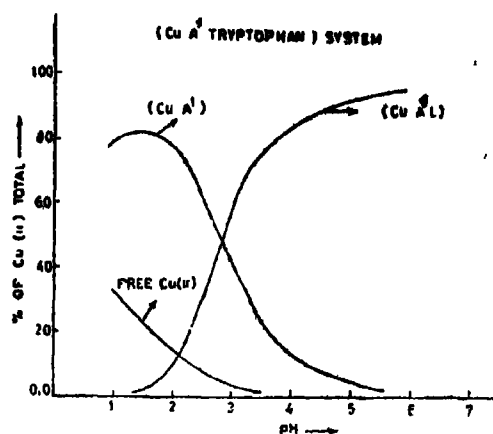
Fig. 1 Variation of concentration of different species with *p*H

Spectral measurement : The spectra were recorded on a Carl Zeiss Specord UV visible spectrophotometer with 1 cm quartz cells using water as solvent. Solutions of concentration 10^{-4} to 10^{-2} mol dm^{-3} were used for uv and visible regions, respectively Spectra of free ligands, mixture of two ligands, $[CuA_2]$, $[CuL_2]$ and [CuAL], prepared by direct mixing of Cu(II) and ligands in required proportions, were obtained. The observed band positions are tabulated in Table 3.

Results and Discussion

It is observed that tryptophan coordinates to the metal ion as bidentate ligand like glycine in binary complexes. The value obtained for $\log K^{Cu}_{CuL}$ in the present study is 8.19 ± 0.09 (Table 1) and is very close to the reported value 8.27 ± 0.05[23]. The position of the d-d band also confirms that the coordination sites in $[Cu(tryptophan)_2]$ are N-O⁻. The observation of the d-d band in $[Cu(tryptophan)_2]$ at 714 nm is very close to the d-d band in $[Cu(gly)_2]$ (712.0 nm) and also confirms that the coordination sites are N-O⁻.

It is observed in the present study that $\Delta \log K$ is positive in the ternary complexes even though the coordination of tryptophan is from aminocarboxylate end. The higher stability of these ternary complexes can be explained by considering following factors. The aminocarboxylate part of tryptophan coordinates with [CuA] and the indole part remains free. This can spread over the bipridyl base part and there may be intramolecular stacking interaction between these two parts which contributes to higher stability.

TABLE 3—ELECTRONIC SPECTRAL BANDS (λnm) OF FREE LIGANDS AND BINARY AND TERNARY Cu(II) COMPLEXES IN AQUEOUS MEDIUM

A^1	233.6	284 1			
A^2	230.4	266.1			
Tryptophan (L^1)	215.1	270.3	277.8	285.7 (sh)	
$[CuA^1_2]$	243.9	303 0	314.5	700	
$[CuA^2_2]$	231.5	275 5	298.5 (sh)	699	
$[CuL^1_2]$	209.2	270.3	277.8	285.7	714.3
A^1+L^1	218.6	244.0 (sh)	285.7	305.3 (sh)	492 0 (sh)
A^2+L^1	222.2	268.5	290 0 (sh)	322.6	496.0 (sh)
$[CuA^1L^1]$	217 4 (sh)	244.0 (sh)	258 0 (sh)	287.8	298.5, 310.3, 457.0 (sh), 682.6
$[CuA^2L^1]$	212.8	270 3	289.9 (sh)	466 0 (sh)	685.0

In mixed ligand complexes [Cu(ATP)(tryptophan)], it was observed by Sigel[23] that tryptophan coordinates through aminocarboxylate end. There is intramolecular stacking interaction between the indole moiety of tryptophan and purine moiety of ATP in these mixed ligand complexes i.e. these complexes can be considered as metal ion bridged stacking adducts. This contributes to the stability of ternary complexes. Due to this stacking interaction charge transfer band observed at 292 nm in a mixture of ATP^{4-}+tryptophan is shifted to 295 nm (lower energy) in the ternary complex [Cu(ATP)-(tryptophan)]. Similar type of stacking interaction is also observed in [Cu(ATP)(bipy)] complexes[24]. In a mixture of ATP^{4-}+bipy there is a new band at 295 nm, which is shifted to 313 nm (lower energy) in [Cu(ATP)(bipy)] ternary complex. This is due to stacking interaction between bipyridyl and the base part of ATP in the ternary complex.

In the present study, we observed a new band at 492 nm in a mixture of tryptophan and bipy This is due to charge transfer interaction between base part of bipy and indole moiety of tryptophan This new band is found to be shifted to 457 nm (higher energy) in mixed ligand complex [Cu(bipy)-(tryptophan)]. This indicates that there is charge transfer interaction between the indole and bipy moiety in the ternary complex also. However, in the mixed complex the charge transfer band is shifted to higher energy region unlike in [Cu(ATP)-(tryptophan)] and [Cu(ATP)(bipy)] complexes where charge transfer band moves to lower energy region. It can be explained by comparing with [Cu(bipy)-(phenylalanine)] wherein it was considered that the phenyl part of alanine can not reach over bipyridyl. In tryptophan also $(CH_2)_2$ chain linking indole part with the nitrogen is as in phenylalanine. However, indole part has two rings. Hence, it may partly reach over bipyridyl and there may be a distant charge transfer interaction requiring higher amount of energy. This shows that the charge transfer interaction in the ternary complex [CuA-tryptophan] is reduced and hence may not contribute to the positive $\Delta \log K$ value.

The positive $\Delta \log K$ in this $N\text{-}O^-$ coordinating ligand can be explained by considering that there is repulsion in the binary complex between the Cu(II) electrons and the indole ring electrons of tryptophan which can come over the metal ion as in case of Cu-phenylalanine, Cu-tyrosine, Cu-dopa. But in ternary complexes due to $M \rightarrow A\ \pi$ interaction the electron density over Cu^{2+} ion is effectively reduced and hence the repulsion is less in ternary complex. This lowering in electron repulsion stabilizes the complex formation and leads to positive $\Delta \log K$ in these ternary complexes even though the coordination is from $N\text{-}O^-$ site[18].

These ternary complexes, involving two ligands of biochemical importance, thus exhibit interesting structural feature leading to stabilization of the ternary complexes.

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Compatibility of Nitrilotriacetic Acid and 3-Acetyl-4-Hydroxy-6-Methyl-2-Pyrone in the Coordination Sphere of Lanthanon Ions

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A study of the competetion of 3-acetyl-4-hydroxy-6-methyl-2-pyrone (dehydracetic acid, DHA) and nitrilotriacetic acid (NTA) in the coordination sphere of lanthanon ions has been carried out by calculating reproportionation constant which relates the stability of the mixed ligand complex to those of the parent complexes formed by the same ligands It has been found that NTA and DHA are incompatible ligands and mixed ligand complexes formed are less stable than either of the parent complexes The fact is also supported by the observed change in free energy occuring during mixed ligand complex formation All these studies have been carried out at 30.0±0 5° and μ=0.1 ($NaClO_4$) in 50% v/v aqueous dioxane medium

3-Acetyl-4-hydroxy-6-methyl-2-pyrone (DHA) has an α-pyrone structure and is a physiologically active compound. It has been used as fungistatic and fungicide, antibacterial agent, toxic and resistant to micro-organisms. 1 : 3 binary complexes of lanthanons with DHA and the mixed ligand complexes of these trivalent ions with DHA and NTA have been studied and the results reported in the present communication. The various metal ions investigated, required to calculate the reproportionation constant and the change in free energies which occurs during mixed ligand complex formation, are La(III), Pr(III), Nd(III), Sm(III) Gd(III), Dy(III), Yb(III) and Y(III).

Experimental

DHA (Koch Light, England) solution was prepared in freshly distilled dioxane (E. Merck). NTA (Riedel) was dissolved in 3-equivalents of NaOH solution and was used as trisodium salt All chemicals and solvents used were of A. R. quality and solutions were prepared in double distilled water. For ternary systems, the following solutions were titrated potentiometrically against a standard solution of tetramethylammonium hydroxide (TMAH) at 30.0 ±0.5° and ionic concentration of 0.1 M $NaClO_4$, maintaining 50% (v/v) dioxane-water medium : (i) 5.0 ml perchloric acid (0.04 M), (ii) 5.0 ml perchloric acid (0 04 M)+0.5 ml NTA (0.02 M), (iii) 5 0 ml perchloric acid (0.04 M)+1.0 ml DHA (0.01 M), (iv) 5.0 ml perchloric acid (0.04 M)+0.5 ml NTA (0.02 M)+0.5 ml metal ion (0.02 M), (v) 5.0 ml perchloric acid (0.04 M)+1.0 ml DHA (0.01 M)+0.5 ml metal ion (0.02 M) and (vi) 5.0 ml perchloric acid (0 04 M)+0.5 ml NTA (0.02 M)+1.0 ml DHA (0.01 M)+0 5 ml metal ion (0.02 M).

The binary systems were studied with 1 : 5 ratio of metal to ligand under identical conditions. For all calculations total volume was reduced from 20 ml to 19.7 ml due to contraction on mixing dioxane with water.

Results and Discussion

Formation constants: The formation constants of the binary complexes of lanthanons with DHA calculated by weighted least squares method of Sullivan *et al*[1] are listed in Table 1.

TABLE 1—FORMATION CONSTANTS OF THE METAL COMPLEXES WITH DHA CALCULATED BY WEIGHTED LEAST SQUARES METHOD AT 30.0±0 5° AND μ=0.1 M $NaClO_4$

Ln(III)	log β_1	log K_2	log β_2	log K_3	log β_3	S_{min}
H^+	6.33	–	–	–	–	–
La	4.75	4.43	9.18	2.94	12.12	0.0468
Pr	4.88	4.55	9.43	3.15	12.58	0.0284
Nd	5 20	4 64	9.84	3.34	13.18	0.0188
Sm	5.44	4 74	10.18	3 49	13.67	0.0037
Gd	5 57	5.16	10.73	3 70	14.43	0.0092
Dy	5 81	5.30	11 11	4.14	15.25	0.0071
Yb	6.30	5 40	11.70	4.91	16.61	0 0580
Y	5.87	5 37	11.24	4.22	15.46	0.0477

In case of ternary systems, it was observed that NTA reacts with lanthanons at lower pH range as found from titration curves of (ii) and (iv) solutions. The titration curves of (iii) and (vi) solutions overlap in the lower pH range whereas at high pH there is divergence of the curves indicating the coordination of DHA with the species [Ln-NTA]. Also, the [Ln-NTA] species have much higher formation constants as compared to lanthanon-DHA complex and hence ligand exchange possibility is eliminated.

The overall reaction may thus be represented as

$$\text{Ln+NTA} \overset{K_{MA}}{\rightleftharpoons} \text{Ln-NTA}$$

$$\text{Ln-NTA+DHA} \overset{K_{MAL}}{\rightleftharpoons} \text{Ln-NTA-DHA}$$

where K_{MAL} is the formation constant of the mixed species and is given by equation

$$K_{MAL}=\beta_{1,1}=\frac{[\text{Ln-NTA-DHA}]}{[\text{Ln-NTA}][\text{DHA}]}$$

S_{min} values having the same significance as χ^2 with k degrees of freedom[8] have also been calculated for all systems.

Reproportionation constants: The stability of the mixed ligand complexes formed is related to the stability of the parent complexes formed by same ligands through reproportionation constant. This correlation is given by the following expression:

$$\beta_{i,j}=K_{\delta}\,\beta_{m,o}^{i/m}\cdot\beta_{o,m}^{j/m}\;[i+j=m]$$

Where K_{δ} is reproportionation constant (Table 2). This constant is a measure of the compatibility of the various ligands in the coordination sphere of a given metal ion.

TABLE 2—FORMATION AND REPROPORTIONATION CONSTANTS AND S_{min} VALUES OF MIXED LIGAND COMPLEXES AT 30.0±0.5° AND μ = 0.1 M $NaClO_4$

Ln(III)	log $\beta^*_{1,0}$ (M-NTA)	log $\beta_{0,1}$ (M-DHA)	log $\beta_{i,j}$ (M-NTA-DHA)	K_{δ}	S_{min}
La	17.65	9.18	13 35	0 871	0.0140
Pr	19.90	9.43	14 09	0 794	0 0465
Nd	19 36	9.84	14 57	0 933	0 0528
Sm	20 51	10.18	15 07	0 537	0 0952
Gd	20 79	10 73	15 67	0 813	0 1596
Dy	21.16	11 11	15 90	0 589	0 0870
Yb	21 73	11 70	16 63	0 832	0 1631
Y	21.73	11.24	15.64	0.144	0 0426

* Values redetermined under present set of conditions [7]

Formational energies: The individual bond strengths M-A and M-L in the complex MA_iL_j can be calculated from the formation constant of the mixed ligand complex and the parent complexes MA_j and ML_i using the following equations:

$$F_A=\frac{RT}{4j}\cdot\ln\beta_{i,j}\frac{\beta_{j,o}}{\beta_{o,i}}$$

$$F_L=\frac{RT}{4}\ln\beta_{i,j}\frac{\beta_{o,i}}{\beta_{j,o}}$$

The bond strengths in the parent complexes MA_m and ML_m are calculated from the equations:

$$F'_A=\frac{RT}{2m}\cdot\ln\beta_{m,o}$$

$$F'_L=\frac{RT}{2m}\cdot\ln\beta_{o,m}$$

The differences in free energies calculated from these equations characterise the changes of M-A and M-L bond energies which occur during mixed ligand complex formation. The results of the present investigations are listed in Table 3.

Discussion

Pure statistical consideration predicts $\beta_{0,1}/\beta_{0,2}$ values as 3.27 and 4.92, respectively for a ligand functioning as bidentate or tridentate in the presence of lanthanon ions[8]. Our results indicate that $\beta_{0,1}$ values are larger than $\beta_{0,2}$ values and their ratio is less than 3.27 in all the cases, suggesting the bidentate nature of DHA.

TABLE 3—FORMATIONAL ENERGIES OF VARIOUS COMPLEXES IN CALS/MOLE

Ln(III)	M-NTA (parent)	M-NTA (mixed)	Change in free energy	M-DHA (parent)	M-DHA (mixed)	Change in free energy
La	6115	6624	509	3182	2631	−551
Pr	6549	6950	401	3303	2818	−485
Nd	6708	7199	491	3411	2901	−510
Sm	7113	7452	339	3529	2995	−534
Gd	7210	7654	444	3719	3210	−509
Dy	7335	7712	377	3851	3310	−541
Yb	7532	8101	569	4056	3428	−628
Y	7532	7504	−28	3896	3338	−558

It may be noted from Table 1 that the value of formation constants for binary complexes increases regularly from lanthanum to ytterbium and no gadolinium break has been observed. Also, the value for yttrium complex is found to be quite close to the value of dysprosium. Depending upon the nature of the ligand, the formation constant values of yttrium complexes are at times close to those of dysprosium complexes and at others close to praseodymium. Because of its size, yttrium should be found near holmium except when lack of ligand field stabilization moves it closer to gadolinium. Probably polarizability effects or/and minor but variable contributions of covalent bonding are responsible for the erratic behaviour of yttrium[4].

Results of the present investigations show that mixed ligand complexes formed are less stable than either of the parent complexes (Tables 2 and 3). M-NTA bond strengths increase while M-DHA bond strengths decrease. The lower stability of the mixed ligand complexes can be explained on the basis of electrostatic considerations. The driving force for the binding of secondary ligand L^- with [MA] should be less than that for the binding of L^- with $[M(aq)]^{3+}$. Further, NTA molecule with a bigger size is expected to produce a greater steric hindrance to the entry of the second ligand in the coordination sphere of the metal ion and decreases the stability to a great extent.

The lower stability of the mixed ligand complexes is also due to incompatible nature of NTA and DHA in the coordination sphere of lanthanon ions and is reflected in the values of reproportionation constant which is less than unity in all the cases. It has been observed that if the geometrical structures and bond types of the parent complexes differ from each other, the ligands are incompatible and the mixed ligand complexes formed are less stable than either of the parent complexes[8]. In such cases, the bonds between the metal ion and one of the ligands become more ionic and the bonds between the metal ion and the second ligand become

more covalent. These effects are of opposite sign and the net energy change may be positive or negative depending upon the nature of ligands and metal ion involved in complex formation[6].

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The Oxidation of Optically Active 3,4-Dihydroxyphenylalanine by Optically Active Cobalt(III) Complexes

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Oxidation of $(-)_D$-3,4-dihydroxyphenylalanine (dopa) by (+)-, (−)-, and racemic $[CoCl(NH_3)(en)_2]Br_2$ was studied by the measurement of oxygen absorbed, optical rotation, and absorption spectrum. The same intermediate which has a large (−) rotation was formed from three optical isomers of the above complex. The configuration of this intermediate is presumed to be a *trans-bis*(ethylenediamine) complex with one molecule of dopa or its oxidation product in the fifth coordination site. The oxidation scheme of dopa by cobalt(III) complexes is discussed.

IN 1920 Yuji Shibata and his elder brother Keita Shibata found an interesting phenomenon exhibited by some complexes of cobalt(III), nickel(II), copper(II) etc[1]. These complexes showed oxidase-like oxidizing actions on some hydroxyflavones like myricetin and polyphenols like pyrogallol. A series of investigation on this subject executed by Y. and K. Shibata and their co-workers proved that these oxidation reactions had a catalytic nature and resembled enzyme actions from the view point of chemical kinetics[2]. During the course of studies Y. Shibata and his co-workers including R Tsuchida reported that chiral organic compounds like $(-)_D$-3,4-dihydroxyphenylalanine (dopa)[3] and $(+)_D$-catechin (3, 3′, 4′, 5, 7-flavapentol)[4] were oxidized with different rates by (+)- and (−)-isomers of chiral cobalt(III) complexes, a phenomenon of so-called asymmetric oxidation. We have been interested in these important and interesting works, and wanted to study more extensively this asymmetric oxidation Our results, which are different from theirs, are reported here[5].

Since the work of Shibata and Tsuchida in 1929[3] Langenbeck *et al*[6] reported the asymmetric oxidation of dopa by copper chelates, and Hatano *et al*[7] studied catalytic oxidation of dopa by poly-α-amino acid-copper (II) complexes. Since dopa is a biologically important substance, there are many reports on it. Recently, Gergely and Kiss[8] studied equilibria of dopa with copper, nickel and zinc in solution and published an extensive review[9].

Experimental

Materials :

The following cobalt(III) complexes were prepared according to the literature methods[10] :

trans-$[CoCl_2(en)_2]Cl$, *cis*-$[CoCl_2(en)_2]Cl$, *cis*-$[CoCl(NH_3)(en)_2]Br_2$, *cis*-$[Co(NH_3)(en)_2(H_2O)]Br_3.H_2O$, $[CoCl(NH_3)_5]Cl_2$ and *cis*-$[Co(NH_3)_4(H_2O)_2]Cl_3$

The resolution of *cis*-$[CoCl(NH_3)(en)_2]Br_2$ was carried out by fractional crystallization of the diastereoisomers with $(+)_D$-bromocamphor-π-sulfonate[11]. The specific rotations of the complex in 0.5% aqueous solutions were $[\alpha]^{25}_{546} = +50.8 \pm 1.0°$ (2 cm cell) and $-50.9 \pm 1.0°$ (2 cm cell), respectively.

The other chemicals including dopa, tyrosine, alanine and phenylalanine were commercial products.

Measurements :

A mixed solution of the substrate, cobalt(III) complex, and phosphate buffer (pH 7 2) was kept at 25° A portion of this reaction mixture was taken out at appropriate time intervals for the measurement of pH, absorption spectrum and optical rotation.

In the latter half of the oxidation reaction, the solution became dark brown in colour with black precipitates (melanin). The precipitates were filtered off and the filtrate was diluted, if necessary, two to four times, and the absorption was measured using quartz cells 2, 5 and 10 mm length. Optical rotatory dispersion (ORD) and circular dichroism (CD) were measured for the solutions prepared similarly. All the measurements were made at 25° on a JASCO ORD/UV-5 recording spectrophotometer equipped with a CD attachment.

The concentrations and amounts of the reaction solutions used were : dopa 1.53×10^{-2} mol/l, 100 ml ; the complex 3.06×10^{-3} mol/l, 25 ml ; phosphate buffer (pH 7.2) 0.2 mol/l, 5 ml, unless otherwise stated.

The amount of cobalt(II) ion formed during the reaction was colorimetrically determined after the following procedures. The solutions used were (−)-dopa (1.2×10^{-2} mol/l, 50 ml), r-$[CoCl(NH_3)(en)_2]Br_2$ (1.2×10^{-3} mol/l, 50 ml) and phosphate buffer [0 2 mol/l (pH 7.2), 50 ml]. One ml of the reaction solution was taken out and mixed with 10 ml of ammonium thiocyanate (50 g/100 ml H_2O) solution and 10 ml of an isoamyl alcohol-ethyl ether (3 : 1) mixture. The mixture was vigorously shaken for 10 min and the optical density of the organic

layer was measured at 610 nm using a quartz cell 1 cm thick.

The amount of oxygen gas absorption during the reaction was measured with Warburg manometer which has a 14∼16 ml reaction vessel. The vessel was shaken at a rate of 60 strokes per min.

Results and Discussion

(1) *Oxidation of racemic dopa* :

Shibata and Tsuchida reported that when racemic dopa was oxidized by (−)-[CoCl(NH_3)(en)$_2$]Br_2 in an aqueous solution, the original negative rotation of the reaction mixture increased to a maximum, then decreased to zero and finally a positive rotation was observed. They interpreted the result in the way that the (−)-complex oxidized the (−)-component of dopa more easily than the (+)-component and a substance with (−)-rotation, an intermediate of the oxidation of dopa, was produced. The intermediate compound was further oxidized, losing its activityand the reaction mixture thus became gradually less negative and finally positive due tothe remaining less oxidizable (+)-dopa.

We tried to reproduce the results of Shibata and Tsuchida[3] and carried out the same oxidation reaction under the same experimental conditions but the result obtained (Fig. 1) was different. In our experiments the negative rotation due to the (−)-cobalt complex decreased to zero without showing a maximum. Before measuring the optical rotation a dilute (1 *N*) acetic acid solution was added to stop the reaction. When the (+)-complex was used, the same result was obtained with opposite rotation No asymmetric oxidation was observed.
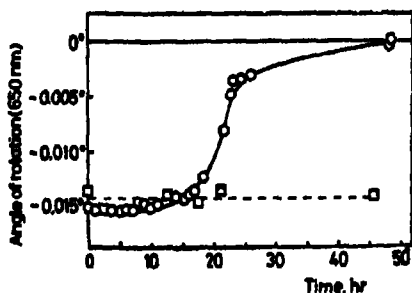
Fig. 1. Change of the angle of rotation during oxidation of r-dopa by (−)-[CoCl(NH_3)(en)$_2$]Br_2 The angle of rotation of the complex solution alone is shown by □. Cell : 1 cm.

(2) *Oxidation of optically active (−)-dopa* :

As the asymmetric oxidation of Shibata and Tsuchida could not be reproduced, we used (−)-dopa instead of racemic dopa and studied its oxidation by (+)-, (−)- and racemic [CoCl(NH_3)(en)$_2$]Br_2. The concentrations of the reactants were the same as given in *Measurements*. Before measuring the optical rotation 1 ml of 1*N* acetic acid solution was added to 2 ml of the reaction mixture to stop the oxidation. The change of the optical rotation observed at 600 nm is shown in Fig. 2. During the reaction of about 20 hr the *p*H of the solution decreased from the initial 7.2 to 6.5. For three isomers of the complexes, optically active and inactive, the rotation of the reaction mixture always decreased with time to the zero value. The two curves shown by the reaction mixture containing the (+)- and (−)-complexes are almost symmetrical to each other in respect of the mixture containing the racemic complex. These results indicate simply loss of the optical activity of (−)-dopa by oxidation, showing no asymmetric oxidation.
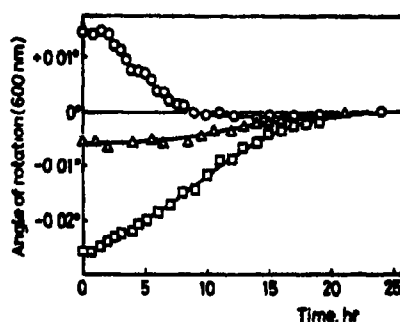
Fig 2. Change of the angle of rotation during oxidation of (−)-dopa by (○)(+)-, (□)(−)-, or (△)r-[CoCl(NH_3)(en)$_2$]Br_2. Cell : 1 cm

In the next experiment no acetic acid was added to the reaction mixture to stop the oxidation before measuring the optical rotation. The results obtained were entirely different from the previous experiments. In the course of the oxidation reaction an identical intermediate, which showed a large negative optical rotation, was formed for (−)-, (+)- and racemic complexes. The amount of the intermediate became maximum in about 10 hr and then gradually decreased (Fig. 3). This intermediate was obviously decomposed by acetic acid because such a large rotation was not observed when acetic acid was used to stop the oxidation.
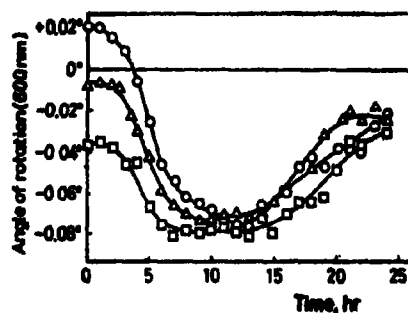
Fig. 3. The same experiment as shown in Fig. 2. Acetic acid was not added to stop the reaction.

To characterize the intermediate further, the ORD curves were measured at several points during the reactions. The results are shown in Fig. 4 which indicates that all the three reactions proceed through the same intermediate with an identical ORD curve. As (+)-, (−)- and r-[CoCl(NH_3)(en)$_2$]Br_2 react in the same way with (−)-dopa, the intermediate is concluded to have no chiral

structure about the cobalt atom and its optical activity should be due to the optically active ligand which is (−)-dopa itself or its partial oxidation product.
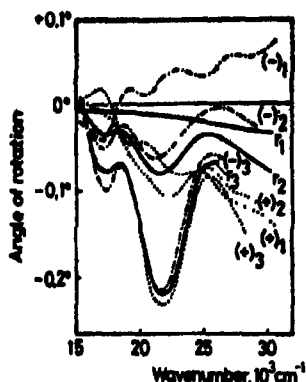
Fig. 4. ORD curves of the same reaction mixtures as shown in Fig. 3. The subscripts 1, 2 and 3 denote the values at 5 min, 4 hr and 10 hr from the beginning of the reaction. The (−), (+), r denote the rotation of the used complexes.

(3) *Determination of cobalt(II) ions formed during the oxidation reaction* :

During the oxidation of (−)-dopa, cobalt(II) ions were detected after a few hr from the beginning. Its amount was determined for the reaction of (−)-dopa and r-[CoCl(NH$_3$)(en)$_2$]Br$_2$. The amount of cobalt(II) ions corresponds closely to the value of optical rotation (Fig. 5), suggesting that the optically active intermediate will be a cobalt(II) complex.
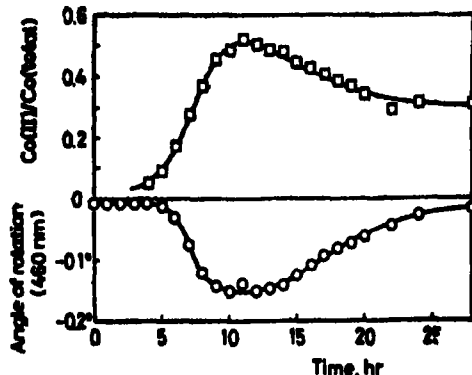
Fig. 5. Relationship between the amount of cobalt(II) ions formed and the angle of rotation during oxidation of (−)-dopa by r-[CoCl(NH$_3$)(en)$_2$]Br$_2$.

(4) *Oxidation of other substrates* :

The interaction and reactivity of r-[CoCl(NH$_3$)-(en)$_2$]Br$_2$ with other substrates were examined spectrophotometrically using L-α-alanine, DL-β-phenylalanine, and L-tyrosine instead of (−)-dopa. These amino acids have partial structures similar to dopa, but have no OH-groups in the *ortho* position.

The mixture of the racemic cobalt(III) complex and the amino acid gave the same absorption spectrum in the visible region during the reaction as that of the cobalt(III) complex alone, that is only the spectral change due to aquation of the complex was observed, no special interaction between the cobalt complex and the substrate being found. This means that carboxylate and amino groups in the side chain of dopa have no effect on the oxidation by the cobalt(III) complex.

(5) *Oxidation of (−)-dopa by various cobalt(III) complexes* :

The oxidation of (−)-dopa was further examined using other *bis*(ethylenediamine) cobalt complexes like *cis*-[Co(NH$_3$)(en)$_2$(H$_2$O)]Br$_3$, *cis*-[CoCl$_2$(en)$_2$]Cl, and *trans*-[CoCl$_2$(en)$_2$]Cl (Fig. 6). The concentrations of the reactants were the same as given in *Measurements*. Clearly, the reaction rates depended on the kind of the cobalt complexes used and the oxidation of (−)-dopa was most rapid for *trans*-[CoCl$_2$(en)$_2$]Cl. All the solutions showed the same characteristic ORD curve as [CoCl(NH$_3$)-(en)$_2$]Br$_2$ at the point of maximum optical rotation. This characteristic ORD curve was also obtained with opposite sign in the reaction of (+)-dopa and *trans*-[CoCl$_2$(en)$_2$]Cl.

Even under nitrogen the reaction between (−)-dopa and *trans*-[CoCl$_2$(en)$_2$]Cl took place and almost the same rotation and ORD curves as in air (Fig. 6) were observed, but the oxidation was suspended halfway without proceeding to the end.
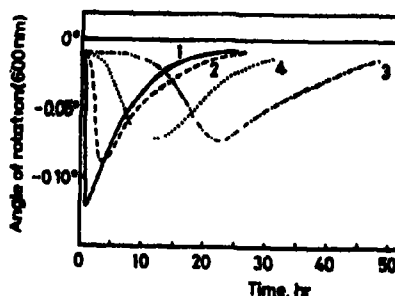
Fig. 6. Oxidation of (−)-dopa by the optically inactive complexes, (1) *trans*-[CoCl$_2$(en)$_2$]Cl ; (2) *cis*-[CoCl$_2$-(en)$_2$]Cl ; (3) *cis*-[Co(NH$_3$)(en)$_2$(H$_2$O)]Br$_3$; (4) *cis*-[CoCl(NH$_3$)(en)$_2$]Br$_2$ (reference). Cell : 1 cm.

Next, instead of a *bis*(ethylenediamine) complex, a mixture of CoCl$_2$ and ethylenediamine solution in the ratio of 1 : 2 was tested for oxidation of (−)-dopa. The same characteristic ORD curve was again observed. Under nitrogen, however, oxidation did not occur and no such ORD curve was observed. This is because oxygen is necessary for the formation of the *bis*(en)cobalt(III) complex from CoCl$_2$ and ethylenediamine and its formation is not possible under nitrogen.

The above fact that *trans*-[CoCl$_2$(en)$_2$]Cl reacts most rapidly with (−)-dopa indicates the structure of the intermediate to be *trans* in relation to the two ethylenediamine molecules. Complexes having the *cis*-*bis*(ethylenediamine) ligands are slow in oxidizing action because it takes some time to transform from the *cis* to the *trans* structure.

Further, cobalt(III) ammines like [CoCl(NH$_3$)$_5$]-Cl$_2$ and *cis*-[Co(NH$_3$)$_4$(H$_2$O)$_2$]Cl$_3$ were studied for

the reaction with (−)-dopa, which have four ammonia molecules instead of two ethylenediamine molecules in the *bis*(ethylenediamine) complexes. The concentrations of the reactants were the same as in *Measurements*. ORD curves, similar to those of the *bis*(ethylenediamine) complexes were observed (Fig. 7) but the peaks at 460 nm and 580nm observed for *bis*(ethylenediamine) complexes shifted to 480~490 nm and ~550 nm (shoulder) in the ammine complexes, respectively.
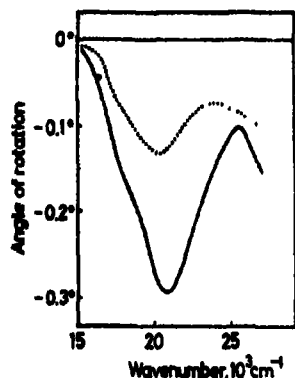
Fig. 7. ORD curves of the reaction mixtures of (−)-dopa and $[CoCl(NH_3)_5]Cl_2$ (full line, 30 min from the beginning) and *cis*-$[Co(NH_3)_4(H_2O)_2]Cl_3$ (dotted line, 20 min).

(6) *Ratio of cobalt(II) to dopa in the reaction intermediate :*

The ratio of cobalt(II) to dopa or its oxidation product in the intermediate was determined using the so-called molar ratio method. First, the concentration of (−)-dopa was kept at 2.94×10^{-3} mol/l (after mixing) while changing the concentrations of *trans*-$[CoCl_2(en)_2]Cl$ from 0.75×10^{-3} to 12×10^{-3} mol/l, and optical rotation at 460 nm was measured. Next, the concentration of the complex *trans*-$[CoCl_2(en)_2]Cl$ was kept at 2.94×10^{-3} mol/l while changing the concentration of (−)-dopa from 0.75×10^{-3} to 12×10^{-3} mol/l. In both the cases, the 1 : 1 ratio of cobalt(II) to dopa was found in the intermediate.

In order to know the effect of phosphate buffer, a KOH solution was used to adjust the initial *p*H of the reaction solution of (−)-dopa and *trans*-$[CoCl_2(en)_2]Cl$ at 7.2. The same ORD curve was observed, indicating that phosphate ion did not participate in the intermediate formation.

(7) *Oxygen uptake during oxidation of (−)-dopa :*

Fig. 8 shows the results of oxygen uptake during the reaction of (−)-dopa with (−)-, (+)- and r-$[CoCl(NH_3)(en)_2]Br_2$. The solutions used were 1.2×10^{-3} mol/l, 1 ml for (−)-dopa, 1.2×10^{-3} mol/l, 1 ml for each cobalt complex, and 0.2 mol/l, 1 ml for phosphate buffer. Three curves agreed with each other within experimental errors and about 2.1 moles of oxygen were consumed for oxidation of one mole of (−)-dopa in 150 hr. No asymmetric oxidation was found.
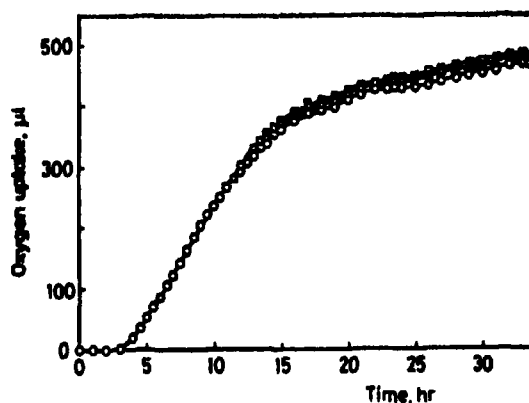
Fig. 8. The oxygen uptake during the oxidation of (−)-dopa by (○)(+)-, (□)(−)- and (△)r-$[CoCl(NH_3)(en)_2]Br_2$.

(8) *Circular dichroism of the intermediate compound :*

The circular dichroism spectra in the reaction of (+)-dopa with *trans*-$[CoCl_2(en)_2]Cl$ and $[CoCl(NH_3)_5]Cl_2$ are shown in Fig. 9. The experimental conditions are the same as those in Figs. 6 and 7, where (−)-dopa was used as the substrate. Three peaks of the CD curve in Fig. 9 are in the longer wavelength region compared with the cobalt(III) complexes of similar types, but it is not yet possible to analyze the curve because information on the CD of optically active cobalt(II) complexes is scarce.
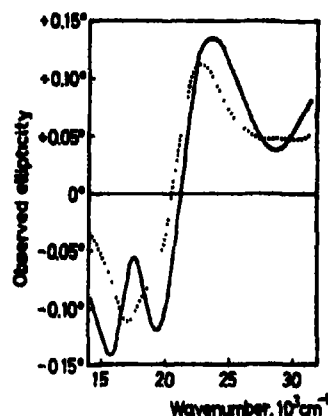
Fig. 9. Circular dichroism spectra observed during oxidation of (+)-dopa by *trans*-$[CoCl_2(en)_2]Cl$ (full line, after 1 hr) and $[CoCl(NH_3)_5]Cl_2$ (dotted line, after 5 min). Cell : 1 cm.

( ) *The structure of the intermediate and the mechanism of the oxidation of (−)-dopa :*

On the basis of the results obtained, the oxidation intermediate of (−)-dopa with a characteristic ORD is presumed to have the following structure :

i) a cobalt(II) complex.
ii) two ethylenediamine ligands in the *trans* position.
iii) ratio of (−)-dopa or its partial oxidation product to cobalt(II) is 1 : 1.

The presumed oxidation mechanism of (−)-dopa by the cobalt(III) complexes is summarized in Fig. 10. In the reaction, first dopa coordinates to the cobalt(III) complex with one of the OH groups of catechol component. The oxidation is initiated by an electron transfer from dopa to cobalt(III) forming a cobalt(II) complex which makes the dissociation of a proton from an OH group easier and increases the hydrogen ion concentration of the reaction medium. This process is possible even under nitrogen but further oxidation of dopa needs oxygen and under nitrogen the reaction stops at this point where a slightly yellow colour appears in the reaction solution.
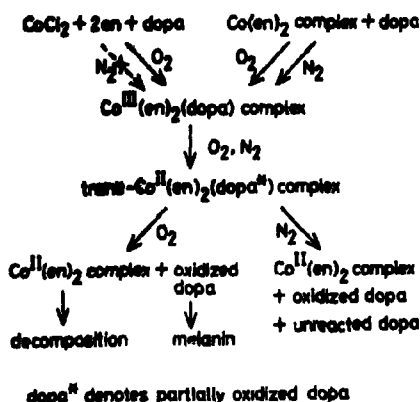
Fig. 10. Oxidation reaction scheme of dopa by cobalt(III) complexes.

Conclusion :

In 1929 Shibata and Tsuchida reported the asymmetric oxidation of dopa by an optically active cobalt(III) complex[3]. Our experiments to reproduce their results failed, but an interesting oxidation reaction of optically active dopa was found which includes the formation of an intermediate, a cobalt(II) complex coordinated by dopa or its partial oxidation product.

In addition to dopa, Shibata with his co-workers studied the oxidation of $(+)_D$-catechin (3,3′,4′,5,7-flavapentol) by optically active (+)- and (−)-$[CoCl(NH_3)(en)_2]Br_2$[4]. In this case they observed that oxygen was absorbed for the system $(+)_D$-catechin + (+)-complex more rapidly than for the system $(+)_D$-catechin + (−)-complex. This fact was confirmed by our unpublished experiments but it is not possible at present to study this problem further.

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Optical Inversion of the *cis*(NO_2), *trans*(N), *cis*(O)-bis(Aminocarboxylato)dinitrocobaltate(III) Ion**

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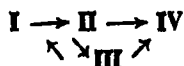
The inversion kinetics of optical isomers of *cis*(NO_2), *trans*(N), *cis*(O)-dinitrobis-(aminocarboxylato)cobaltate(III) ions, containing various α- and β-amino acid residues (glycine, S-aminobutyric acid, S-leucine and β-alanine) have been studied. The inversion process was followed polarimetrically in sodium nitrate solution, between 55 and 95° (I = 0.15). It was established that the inversion of the *cis*(NO_2), *trans*(N), *cis*(O) optical isomer of the dinitro-bis(β-alaninato)cobaltate(III) ion, in which β-alanine forms six-membered ring, is faster than the inversion of all other corresponding isomers containing five-membered aminocarboxylato ligand rings. In addition, it was assumed that the *cis*-(NO_2), *trans*(N), *cis*(O) optical isomers of dinitrobis(aminocarboxylato)cobaltate(III) complexes containing α- and β- aminocarboxylato residues, respectively, rearrange via an intramolecular mechanism which involves the bond rupture between one end of the aminocarboxylato ligand and the central ion.

IN our previous papers[1] the synthesis of several series of geometrical isomers of complexes of *bis*-(aminocarboxylato) dinitrocobaltate(III) type, containing various α- and β-amino acid residues, respectively, were described. In another paper[2], we also reported the studies on the isomerization reactions of four geometrical isomers of the diglycinatodinitrocobaltate(III) ion (Fig. 1). The results of experiments between 65 and 95° in neutral solution are consistent with the stoichiometric mechanism :

$$\mathrm{I} \longrightarrow \mathrm{II} \longrightarrow \mathrm{IV}$$
$$\nwarrow \searrow \mathrm{III} \nearrow$$

In addition, we investigated[3] the racemization of the isomer I, i.e. of $(+)_{589}$-*cis*(NO_2),*cis*(N),-*cis*(O)-diglycinatodinitrocobaltate(III) ion.

Continuing these investigations, the inversion reactions of the optical isomers of *cis*(NO_2)-, *trans*(N),*cis*(O)-*bis*(aminocarboxylato)dinitroco-baltate(III) ions (IV) containing various α- and β-amino acid residues are described in the present communication. The inversion process was followed polarimetrically in sodium nitrate solution (I=0.15) between 55 and 95°.

Experimental

Preparation of the complexes :

All the investigated optical isomers were prepared as described earlier : glycinato (gly) complexes[1,2], β-alaninato (β-ala) enantiomers[4], S-aminobutyrato (S-abu) diastereomers[5] and S-leucinato (S-leu) diastereomers[1].

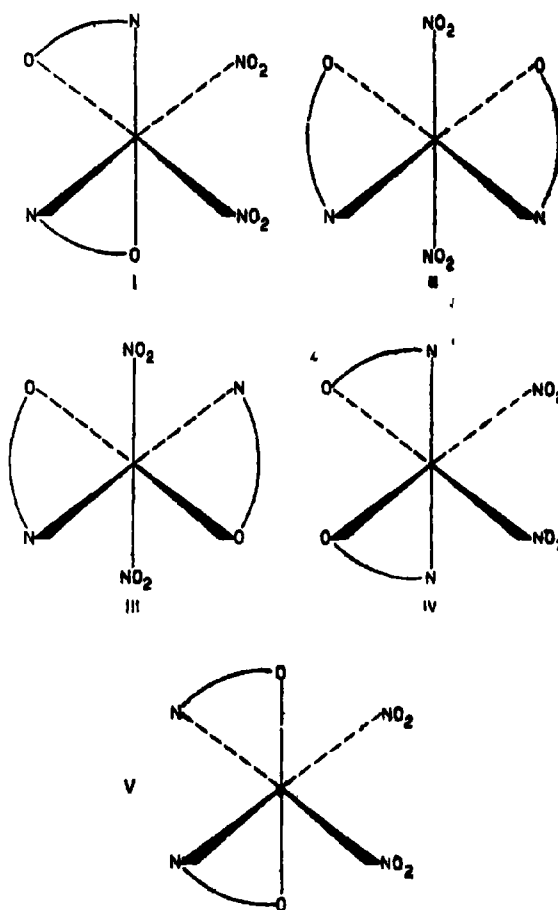



Fig. 1. The five geometric isomers of diglycinatodinitro-cobaltate(III) ion. Isomers I-IV have been isolated. Isomer V has not been observed.

**Part of these results was presented at the 8th Conference on Coordination Chemistry in Smolenice (Bratislava), Czechoslovakia, 1980.

Kinetic experiments :

Inversion reactions were studied by heating 0.5 cm^3 of aqueous solutions (having a concentration of 0.05 mol/dm^3) of the corresponding enantiomer or diastereomer, in glass ampules placed in an ultrathermostat (Thermostat Type NBE, Medingen, Dresden). Since paper chromatographic studies had shown that the $(-)_{589}$-*cis*(NO_2)-*trans*(N)-*cis*-(O)-enantiomer of dinitrobis(β-alaninato)cobaltate(III) ion is partially decomposed at temperatures above 80°, the corresponding kinetic racemization experiments were carried out at 55, 65, 75 and 80°, respectively. The ionic strength was 0.15, adjusted with sodium nitrate. In course of the kinetic experiments the ampules were taken out from the thermostat at given time intervals and quickly cooled in ice water. Solutions from the ampules were quantitatively transferred into a 10 cm^3 volumetric flask, which was then filled up to the mark with distilled water. Optical rotations of the solutions obtained were measured in a Perkin Elmer 141 MC Digital Polarimeter at sodium line (±0.002°).

In each experiment, it was checked whether the substance studied had either partially decomposed or isomerized in course of heating at the above mentioned temperatures. This was accomplished by paper chromatographing the heated solutions or by taking their visible spectra ; the R_f values as well as the electronic spectra thus obtained were compared with those obtained with the samples of substances which had not been heated.

Evaluation of the kinetic parameters :

In case of a reversible first order reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad \dots (0)$$

the change of concentration of the component B with time is given by the equation :

$$[B]=[\bar{B}]/1+e^{-(k_1+k_{-1})t} \qquad \dots (1)$$

where [B] denotes the concentration of the component B, and $[\bar{B}]$ its equilibrium concentration[6].

Expanding $e^{-(k_1+k_{-1})t}$ as a power series, gives :

$$[B]=[\bar{B}]\left\{\frac{(k_1+k_{-1})t}{1!}-\frac{(k_1+k_{-1})^2t^2}{2!}+\dots\right\} \qquad \dots (2)$$

Dividing the equation (2) with t the following is obtained :

$$\frac{[B]}{t}=[\bar{B}]\left\{\frac{(k_1+k_{-1})}{1!}-\frac{(k_1+k_{-1})^2\,t}{2!}+\right\} \dots (3)$$

The above equation shows that the graphic representation of $\frac{[B]}{t}$ (the ordinate) as a function of t (the abscissa) in the beginning of the reaction, i.e. when in the equation (3) all the members except the first two can be neglected, gives a straight line with the intercept $[\bar{B}](k_1+k_{-1})$ and the slope $-[\bar{B}]\frac{(k_1+k_{-1})^2}{2}$.

This procedure is analogous to that for irreversible first order reactions described by Hall *et al*[7].

$$\text{Since } [\bar{A}]+[\bar{B}]=[A_0] \qquad \dots (4)$$

(where $[A_0]$ denotes the initial concentration of the component A), and

$$\frac{[\bar{B}]}{[\bar{A}]}=\frac{k_1}{k_{-1}}=K \qquad \dots (5)$$

it follows that from the data obtained by the procedure described, k_1, k_{-1} and $[\bar{B}]$ can be calculated in the following manner :

$$k_1=\frac{\text{intercept}}{[A_0]} \qquad \dots (6)$$

$$k_{-1}=-\frac{2(\text{slope})}{\text{intercept}}-k_1 \qquad \dots (7)$$

$$[\bar{B}]=-\frac{(\text{intercept})^2}{2(\text{slope})} \qquad \dots (8)$$

The change in the concentration of the component B with time in course of the reaction was determined in the usual way by measuring the optical rotation of the solutions :

$$[B]=[A_0]\frac{(\alpha_A-\alpha_t)}{(\alpha_A-\alpha_B)} \qquad \dots (9)$$

where α_A and α_B denote the optical rotations of the solutions of pure A and B components, respectively, and α_t is the optical rotation of the investigated solution in course of the reaction.

Chromatographic investigations :

Paper chromatography of the investigated substances was carried out in a glass cylinder, height 50 cm, diameter 22 cm, by ascending method, on Whatman No. 1 paper strips (3×30 cm). The development was performed at 20±2°, the solvent system being placed into the cylinder 1 hr before development. The solvent system used was a mixture of ethyl acetate : ethanol : water (70 : 20 : 10). The solvent front travelled about 22 cm and the developing time was about 6 hr. The substances were detected by dipping the developed paper strips into ammonium sulphide solution (~2 mol/dm^3).

Absorption spectra :

Absorption spectra of the investigated substances in the visible region were taken in aqueous solutions on a Perkin-Elmer 137-UV spectrophotometer.

Optical rotation :

Optical rotation of the isomers obtained was measured at 589 nm on a Franz Schmidt & Haensch Model S Polarimeter ; the measurements were performed at room temperature in 10 cm^3 cells with aqueous solutions, the concentrations ranging from 0.1 to 0.2 g per 100 cm^3.

Reagents :

All reagents used were of "puriss" reagent grade purity. Sodium hexanitrocobaltate(III) was a product of E. Merck, AG, Darmstadt, or Fluka AG, Buchs. S-Aminobutyric acid and S-leucine were the products of Fluka AG, Buchs, whereas glycine and β-alanine were obtained from Kemika, Zagreb.

Results and Discussion

The observed first order rate constants are given in Table 1, and the corresponding activation enthalpies and entropies in Table 2 (see also Fig. 2 and 3).

TABLE 1—FIRST ORDER INVERSION RATE CONSTANTS (k_{in} . 10^6 sec^{-1}) OF OPTICAL ISOMERS OF *cis*(NO_2),*trans*(N), *cis*(O)-BIS(AMINOCARBOXYLATO)DINITROCOBALTATE(III) ION*

Complex	Temperature (°C)											
	40	45	50	55	60	65	70	75	80	85	90	95
Λ-(+)$_{589}$-[Co(NO_2)$_2$ gly$_2$]$^-$	–	–	–	–	1 3±0.1	2.8±0 2	3.5±0.2	11±1	15±1	–	62±6	–
Λ-(+)$_{589}$-[Co(NO_2)$_2$ (S-abu)$_2$]$^-$	–	–	–	–	–	2 1±0 5	–	5 4±0 2	–	14±1	–	43±1
Λ-(+)$_{589}$-[Co(NO_2)$_2$ (S-leu)$_2$]$^-$	–	–	–	–	–	2 1±0 5	–	5.5±0 3	–	15±1	–	47±1
Δ-(–)$_{589}$-[Co(NO_2)$_2$ (S-abu)$_2$]$^-$	–	–	–	–	–	1.8±0.5	–	4.8±0 6	–	12±1	–	36±1
Δ-(–)$_{589}$-[Co(NO_2)$_2$ (S-leu)$_2$]$^-$	–	–	–	–	–	1.0±0.4	–	3.1±0.3	–	7.7±0.2	–	21±1
Δ-(–)$_{589}$-[Co(NO_2)$_2$ (β-ala)$_2$]$^-$	–	–	–	14±2	–	30±3	–	70±4	120±20	–	–	–
Λ-(+)$_{589}$-*cis, cis, cis*-[Co(NO_2)$_2$gly$_2$]$^-$	120±5	140±10	150±5	170±10	–	–	–	–	–	–	–	–

* The observed rate constants are given in the form of $X \pm t(P;f)\frac{\sigma}{\sqrt{n}}$, where X represents their mean values obtained by the least squares method, t(P ; f) is student's factor for P = 95%, f = n – 2 degrees of freedom and $\frac{\sigma}{\sqrt{n}}$ standard deviation of the mean (J. M. Wilson *et al*, Experiments in Physical Chemistry, II Ed., Pergamon Press, Oxford, 1968, p 364)

TABLE 2—ACTIVATION PARAMETERS OF INVERSION REACTIONS OF OPTICAL ISOMERS OF *cis*(NO_2),*trans*(N),*cis* (O)-*bis*(AMINOCARBOXYLATO)-DINITROCOBALTATE(III) ION

Complex	ΔH^* k cal mol^{-1}	$\Delta S^*_{78^\circ}$ k cal $mol^{-1}K^{-1}$
Λ-(+)$_{589}$-[Co(NO_2)$_2$gly$_2$]$^-$	29 7	3 91
Λ-(+)$_{589}$-[Co(NO_2)$_2$(S-abu)$_2$]$^-$	24 0	–11 9
Λ-(+)$_{589}$-[Co(NO_2)$_2$(S-leu)$_2$]$^-$	24 6	–10.1
Δ-(–)$_{589}$-[Co(NO_2)$_2$(S abu)$_2$]$^-$	23.6	–13 3
Δ-(–)$_{589}$-[Co(NO_2)$_2$(S-leu)$_2$]$^-$	24 4	–11 8
Δ-(–)$_{589}$-[Co(NO_2)$_2$(β-ala)$_2$]$^-$	18 5	–24.6
Λ-(+)$_{589}$ *cis, cis, cis*-[Co(NO_2)$_2$gly$_2$]$^-$	3 87	–64.1^a

^{a} For 45°

It can be seen from these data that the inversion rate of *cis, cis, cis*-isomer is very much greater than that of the *cis*(NO_2),*trans*(N),*cis*(O)-isomer. This is in accordance with the rather low activation enthalpy of the former isomer, which amounts to 3.87 k cal mol^{-1} [the corresponding values for the *cis*(NO_2), *trans*(N), *cis*(O)-complexes, which also contain α-aminocarboxylato ligands, are between 23.6 to 29.7 k cal mol^{-1}]. In addition, the *cis, cis,*-*cis*-isomer has a highly negative activation entropy ($\Delta S^*_{45}{}^\circ = -64.1$ k cal $mol^{-1}K^{-1}$) but that is not the case with the other isomer ($\Delta S^*_{78}{}^\circ = -13.3$ to 3.91 k cal $mol^{-1}K^{-1}$) On the basis of these, one can conclude that the inversion mechanisms of the two isomers are different As is known[6], an intramolecular mechanism without bond rupture, the trigonal twist mechanism, might account for the low enthalpy and the highly negative entropy of activation. Because of this, we assumed in our earlier paper[3] such a mechanism for the racemization process of the *cis,cis,cis*-isomer. This hypothesis is supported by the fact that an examination of the stereochemistry of the two investigated isomers reveals that the *cis cis,cis*-isomer can theoretically racemize by a trigonal twist whereas the inversion of the *cis*(NO_2),*trans*(N),*cis*(O)-isomer by a twist mechanisms is not possible.

Fig. 2. A typical plot of log α vs time [obtained during the racemization of Δ-(–)$_{589}$-*cis* (NO_2)$_2$-*trans*(N), *cis* (O)-*bis*(β-alaninato)dinitrocobaltate(III) ion].

From the data obtained it can also be seen that the optical inversion of the *cis*(NO_2),*trans*(N),-*cis*(O)-complex containing β-alaninato ligands is considerably faster in comparison to the complexes

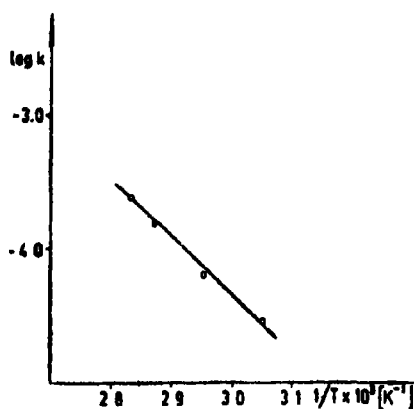



Fig. 3. A typical plot of log k vs $\frac{1}{T}$ [obtained for racemization process of Δ-$(-)_{546}$-*cis*(NO_2),-*trans*(N),-*cis*(O)-*bis*(β-alaninato)dinitrocobaltate(III) ion].

of the same geometrical configuration containing α-aminocarboxylato ligands. This is in accordance with its relatively lower activation enthalpy, as well as with the known fact[9] about greater stability of five-membered rings in comparison to six-membered ones. On the basis of this one could assume that the optical inversion of the investigated complexes takes place by bond rupture between aminocarboxylato ligand and Co(III). It is, however, unlikely that duringthis process a complete chelate ligand dissociation occurs because of relatively modest activation enthalpies (not higher than 30 k cal mol^{-1}) In addition, if such a complete dissociation happens a noticeable complex decomposition would be expected. That was never observed. In this connection, it seems more probable that under the labilising influence of the *trans* NO_2-group, the Co-O bond is broken rather than the Co-N bond (from aminocarboxylato ligand).

The assumed bond rupture intramolecular mechanism is supported by the fact that the activation energy for the substitution process of the NO_2-groups in hexanitrocobaltate(III) ion by aminocarboxylato ligand, for which reaction a dissociation mechanism is accepted, amounts to about 37 k cal mol^{-1} [10], which is a much higher value compared to the values obtained in the present study. Finally, the proposed mechanism is also in accordance with the results obtained by York[11], who established that an exchange involving $^{15}NO_2^-$ and *cis*-Na[Co$(acac)_2(NO_2)_2$] is extremely slow.

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The Deuterium Isotope Effect on the Pfeiffer Effect in Optically Labile Coordination Compounds

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THE Pfeiffer Effect[1] is the change in optical rotation of an optically active system (usually a solution of one enantiomer of an optically active compound, called the "environment substance"), upon the addition of a racemic mixture of a dissymmetric, optically labile coordination compound. Considerable work has been done on this effect by Brasted, Yoneda, Brittain, Kirschner and others[2-11], and several proposed mechanisms to explain it have been described in an excellent review by Schipper[12].

The Pfeiffer effect has been utilized for the study of the resolution and racemization of optically active coordination compounds[13] and for studies of the optical properties of complexes which are extremely labile and which racemize very rapidly[14]. Recent work[15,16] has also been done on applying the Pfeiffer effect to the determination of absolute configurations of optically active complexes which are also optically labile and organic compounds and on explaining the nature of the "equilibrium displacement" mechanism proposed for the effect. In this paper further work is described on the nature and mechanism of the Pfeiffer effect and on the utilization of the deuterium isotope effect to assist in the elucidation of the mechanism.

The equilibrium displacement mechanism for the Pfeiffer effect :

It has been proposed by Dwyer *et al*[3] that an equilibrium exists between the enantiomers of a racemic mixture of an optically labile, dissymmetric complex in solution, with the equilibrium constant being equal to unity. However, in the presence of an appropriate optically active environment substance (one which will cause the Pfeiffer effect to occur and which will not displace a coordinated ligand during the time required for the appearance of the Pfeiffer effect), this equilibrium is shifted toward one of the enantiomers, with the equilibrium constant becoming greater or less than 1, depending on the direction of the shift.

If such a shift occurs, it should be possible to identify the enantiomer produced in excess by means of techniques such as optical rotatory dispersion and circular dichroism, as well as by a "time" experiment (see below). For example, Fig. 1 shows the circular dichroism spectrum of $(+)_D[Cr(ox)_3]^{3-}$ in water along with the Pfeiffer circular dichroism spectrum of D,L-$[Cr(ox)_3]^{3-}$ in water containing *d*-cinchonine hydrochloride as the environment substance (ox= oxalate anion). It can be seen that the two spectra are essentially the same, the difference in intensity between them being due to the different concentrations of the optically active complex ion in solution in the two cases.
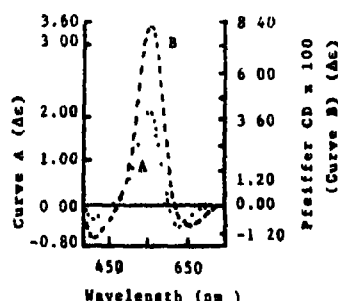
Fig. 1. (A) Circular dichroism spectrum of $(+)_D[Cr(ox)_3]^{3-}$ in H_2O (B) Pfeiffer circular dichroism spectrum of *D,L*-$[Cr(ox)_3]^{3-}$ in water containing *d*-cinchonine hydrochloride (all measurements at 23°).

The "time" experiment referred to above is described in Fig. 2. In this figure it can be seen that the optical rotation of *levo*-malic acid does not change with time. However, when *D,L*-$[Ni(o\text{-}phen)_3]^{2+}$ is added to the solution (at time=0),
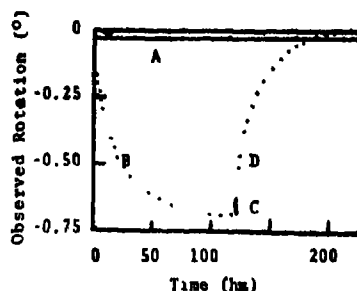
Fig. 2. The "time" experiment. The Pfeiffer effect and subsequent racemization in water of *D,L*-$[Ni(o\text{-}phen)_3]Cl_2$ with *levo*-malic acid as the environment substance. (A) *Levo*-malic acid in water ; (B) *Levo*-malic acid + *D,L*-$[Ni(o\text{-}phen)_3]Cl_2$; (C) the system in (B) + added *dextro*-malic acid after 123 hr ; (D) Racemization of the system in (C) (of the excess *L*-$[Ni(o\text{-}phen)_3]Cl_2$ produced via the Pfeiffer effect).

the Pfeiffer effect develops, with its maximum being attained at about 120 hr (*o*-phen=*ortho*-phenanthroline). If, at that time, exactly the same concentration of *d*-malic acid is added to the system, then this has the effect of eliminating or "optically neutralizing" the optically active environment, with the result that the excess of the *levo* enantiomer of

the complex undergoes racemization until the optical rotation of the substance disappears. Note however that the nickel-*ortho*-phenanthroline complex retains its integrity throughout the Pfeiffer effect experiment, as evidenced by the fact that there is no change in the uv-visible spectrum of the complex throughout the entire "time" experiment. All this provides considerable support for the mechanism which proposes that one enantiomer of the complex is produced in excess during the appearance of the Pfeiffer effect.

It should be noted that, in Fig. 2, if the *d*-malic acid had not been added, then curve B would continue parallel to the horizontal axis until decomposition begins. This permits the study of many optical properties of extremely labile complexes which heretofore could not be studied because the racemization rate is so rapid that any resolved compounds would racemize too quickly to be studied. With the displaced equilibrium mentioned above continuing for some time, the excess of one enantiomer can be studied with regard to recemization rate, optical rotatory dispersion, circular dichroism, etc. This has already been achieved with certain very optically labile complexes[14].

A proposed explanation for the displacement of the equilibrium between the complex enantiomers, which is postulated to occur during the Pfeiffer effect, is that hydrogen bonding occurs preferentially between electronegative atoms of an environment substance of a given absolute configuration and the π-electron clouds of the ligands of one enantiomer of the complex[15]. Such hydrogen bonding interactions to π-electron clouds of aromatic and unsaturated systems are known to occur with organic molecules[17,18].

This proposal is a most attractive one from several standpoints. First of all it provides an explanation for the chiral discrimination which is observed to occur for the Pfeiffer effect, since molecular models of the proposed system indicate that S-malic acid, for example, fits quite well into the Δ_{σ_3} propeller system of the $[Ni(o\text{-phen})_3]^{2+}$ enantiomer with no strong non-bonded hydrogen interactions, whereas the R enantiomer of malic acid in the same propeller system shows two strong non-bonded hydrogen inter. ctions. Consequently, the Δ_{σ_3} configuration is stabilized by S-malic acid, resulting in anequilibrium shift in favour of the Δ_{σ_3} enantiomer.

Also, the initially unexpected behaviour of Pfeiffer-active systems with *p*H changes is explained well by this proposal. One might expect that with increasing *p*H, Pfeiffer activity would increase, since chiral recognition by an optically active complex cation of an anionic environment substance (e.g., *levo*-malate ion) would be expected to be greater than that for the same complex cation and a neutral environment substance (e.g., *levo*-malic acid). In fact, the opposite behaviour is observed, with the Pfeiffer activity undergoing a marked decrease with an increase in *p*H. This can be explained by the hydrogen bonding proposal, since an increase in *p*H will result in removal of the carboxylic hydrogens, thus diminishing the ability of the proposed hydrogen bonding to occur[15].

The Deuterium isotope effect on the Pfeiffer effect:

If the hydrogen-bonding mechanism proposed above has validity, it should be possible to observe a deuterium isotope effect in the system which utilizes S-malic acid as an environment substance, since, in D_2O, the hydrogens of malic acid capable of undergoing hydrogen bonding would be exchanged for deuterium. The effects of "deuterium bonding" compared to hydrogen bonding should be observable in at least two ways—(a) an expected decrease in the rate of appearance of the Pfeiffer effect due to slower "deuterium bonding" effects, and (b) a diminution in the magnitude of the Pfeiffer effect because of the lesser ability of "deuterium bonding" to occur (compared to hydrogen bonding) because of weaker electrostatic interactions.

Consequently, the entire Pfeiffer effect experiment utilizing D,L-$[Ni(o\text{-phen})_3]^{2+}$ and S-$(-)_D$malic acid was performed using D_2O as a solvent in place of water Fig 3 shows the results of this experiment. Curve B is the Pfeiffer effect for the system in water and curve A is that for the system in D_2O It can be seen from Fig 3 that the rate of appearance of the effect in D_2O is significantly less than that observed in H_2O. It can also be seen that the magnitude of the effect in D_2O is considerably less than in H_2O — both results being in accord with what would be expected if hydrogen bonding plays a significant role in the Pfeiffer effect.
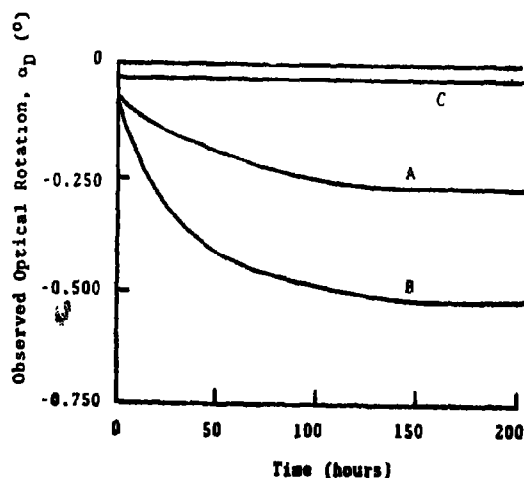
Fig. 3. The deuterium isotope effect on the Pfeiffer effect (A) D,L-$[Ni(o\text{-phen})_3]Cl_2$ (0.05 *M*) + *levo*-malic acid (0.05 *M*) in D_2O; (B) D,L-$[Ni(o\text{-phen})_3]Cl_2$ (0.05 *M*) + *levo*-malic acid (0.05 *M*) in H_2O; (C) *levo*-malic acid (0.05 *M*) in H_2O.

Experimental

ORD and CD spectra were determined on a Cary-60 spectropolarimeter using a CD attachment for the CD spectra. Optical rotations at single wavelengths were determined on a Perkin-Elmer 141

photoelectric polarimeter. The designations "R" and "S" refer to the absolute configurations of organic compounds using the system developed by Cahn, Prelog and Ingold[19,20]. The optically active organic compounds used as environment substances were purchased in the purest forms available and their optical rotations were checked against the literature values. The D,L-[Ni(o-phen)$_3$]Cl$_2$ complex was synthesized according to the method of Kauffman and Takahashi[21]. The D_2O was purchased as reagent grade material in greater than 99% purity. The Pfeiffer effect studies were carried out at room temperature in solutions in which the concentrations of the complex and environment substance were 0.02 *M* and 0.04 *M*, respectively (Fig. 2), and 0 05 *M* in each (Fig. 3)

Conclusions :

Evidence is presented herewith in support of a generalized "equilibrium displacement" mechanism for the Pfeiffer effect and for the "hydrogen bonding" mechanism to explain this proposed equilibrium displacement. In particular, the deuterium isotope effect on the Pfeiffer effect occurs in a manner consistent with the proposed hydrogen bonding between labile protons (or deuterons) of the environment substance and the π-electron clouds of the ligands of optically labile, racemic complexes, thus modifying their ability to undergo configurational changes and resulting in an equilibrium displacement between the enantiomers of the complex.

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Coordination Chemistry of Technetium as Related to Nuclear Medicine

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Significant advances have been made in the area of technetium coordination chemistry during the last five years. The main driving force behind this recent surge of interest in the field has been due to the practical application of technetium-99m in the rapidly growing speciality of nuclear medicine. Technetium-99 is one of the products of nuclear fission reactions, but it was the development of the molybdenum-99-technetium-99m generator about two decades ago that provided the basis for the development of radiopharmaceuticals routinely used in modern diagnostic applications. The chemistry of this element has proven to be quite rich owing to its multiple oxidation states and variable geometry; this can be attributed to its position in the middle of the periodic table. Diagnostic radiopharmaceuticals comprise predominantly III, IV and V oxidation states of Tc and involve a variety of coordination complexes. Even though the chemistry of Tc has been slow to evolve, recent synthetic advances have provided a more scientific basis for the study of a number of compounds with diverse coordination geometries and structures. Ligands with oxygen, nitrogen, and sulfur donor atoms have been utilized to elucidate various aspects of the coordination chemistry of Tc Single crystal X-ray structural analysis has been extensively used to characterize Tc complexes and thus construct a firm foundation for the study of synthetic and mechanistic aspects of the chemistry of this element.

EVEN though technetium has been observed in some stellar materials and despite some evidence suggesting that a continuous production of the element is taking place in the universe[1], evidence for the occurrence of primordial terrestrial technetium has not yet materialized despite the extensive searches using sophisticated radiochemical procedures. On a geological time scale, all isotopes of this element are unstable and thus throughout the early history of chemistry, no technetium was avilable for study. Artificial production of technetium in minute quantities was reported by Perrier and Segre in 1937[2], and chemical quantities became available in the early 1960's (*ca* \$3000/g) At the present time ^{99}Tc is produced in kilogram amounts as a fission product and is available at about \$50 per g. ^{99}Tc is a soft beta emitter (β^- max 0 292 MeV) with a 2.13×10^5 yr half-life and thus presents only a minor radiation hazard. Milligram quantities can safely be manipulated by following a few simple precautions. Virtually all chemical studies so far have employed ^{99}Tc.

Since the mid 1970's there has been a dramatic surge of activity in the area of synthetic and structural chemistry of technetium. This is attributable to the desire of inorganic chemists to acquire a basic understanding of the chemistry of this sparsely studied element. A very great driving force has been provided by the widespread use of technetium-99m in diagnostic nuclear medicine procedures and by the ever growing realization that further advances in the area of ^{99m}Tc radiopharmaceuticals will greatly depend on basic research effort on solution chemistry, coordination complexes, and mechanistic studies of Tc compounds[3].

Uses in nuclear medicine :

To carry out diagnostic nuclear medicine procedures, a "radiopharmaceutical" (some chemical form of a gamma emitting radionuclide) is injected into a patient and the biodistribution of the radiopharmaceutical is monitored by suitable external imaging devices such as a gamma camera. Among the few radionuclides available for these applications, ^{99m}Tc has, by far, the optimum properties and is clearly the "ideal" radiotracer[4]. The monoenergetic gamma emission of 140 keV is well suited for use with the present day gamma cameras. This energy provides excellent penetration from deep seated organs in the body and the loss during collimation is minimal. A total lack of beta emission results in the absence of unnecessary absorbed radiation dose to the patient. The 6.02 hr half-life cuts down the radiation dose further by minimizing continued patient exposure after completion of the diagnostic procedure. Because of reduced radiation dose, large amounts of radioactivity can be administered in order to provide good resolution and increased information content in the collected images. Very frequent repetition of studies is also facilitated. ^{99m}Tc is inexpensive and is readily available as $^{99m}TcO_4^-$ with the advent of the ^{99}Mo/^{99m}Tc generator[5,6]. Of equal importance is the fact that the varied chemistry of technetium in its many oxidation states allows the incorporation of ^{99m}Tc into a variety of radiopharmaceuticals that are specific for different organs[3]. Without the possibility of appropriate chemical manipulations, the preeminence of ^{99m}Tc among the medically useful radionuclides would not have been established. The use of ^{99m}Tc for diagnosis has proven so successful

that in the U. S. alone at present more than 10 million nuclear medicine scans are conducted annually utilizing some chemical form of this radionuclide.

Technetium-99m radiopharmaceuticals ·

A variety of ^{99m}Tc imaging agents are in current use. These are generally coordination complexes of technetium prepared at very dilute concentrations dictated by the use of generator produced "no-carrier-added" $^{99m}TcO_4^-$. The structure and chemical reactivity of these agents have only recently begun to be adequately characterized. Only nanogram quantities of ^{99m}Tc are present in most formulations and this makes most chemical measurements difficult, if not impossible. The majority of clinically used agents are produced with the use of commercially available derivatizing "kits" that generally contain a reductant (usually Sn^{2+} ion) in the presence of a complexing agent. Based on their biological behaviour, ^{99m}Tc labeled compounds can be categorized as belonging to two broad classes :

(i) agents where ^{99m}Tc functions as a true tracer, that is, the labeled compound retains its biodistribution after being tagged with ^{99m}Tc. This category includes cells, particles, macromolecules and bioactive compounds. The presence of technetium produces small or no perturbation,

(ii) compounds whose biodistribution to a large extent is determined by the properties of the complex itself and by the nature of the particular technetium center. This class comprises most low molecular weight technetium coordination complexes that are in use at the present time.

The lack of a clear understanding of the structure-activity relationships of technetium labeled compounds has greatly hampered the design of agents with predictable biological behaviour and that could be targeted to specific organs and tissues with a high degree of selectivity. A more rational approach (than the empirical ones used in the past) that is being followed to some extent presently involves first the preparation and chemical characterization of macroscopic amounts of a ^{99}Tc complex and then the manipulation of preparative conditions to successfully synthesize an identical complex at the no-carrier-added levels of $^{99m}TcO_4^-$ encountered in the generator eluates. The correspondence at the two concentration levels can usually be established by sensitive chromatographic methods (especially HPLC) and various other techniques including biological studies using small animals. Much concern has been expressed regarding the translation of results obtained at the carrier level of ^{99}Tc to those at the no-carrier-added level of ^{99m}Tc. In general, the differences are explainable and the correspondence is fairly satisfactory.

A number of agents labeled with ^{99m}Tc including inorganic and organic ligands, colloids and particles, cellular elements of blood, and various biological macromolecules are routinely used in present day diagnostic nuclear medicine[6]. A brief list which includes potential new radiopharmaceuticals as well is as follows :

(i) phosphates, diphosphonates and imidodiphosphonates for the imaging of the skeletal system,

(ii) EDTA, DTPA, gluconate, glucoheptonate, ascorbate, dimercaptosuccinic acid, citrate and cysteine for kidney imaging and for determination of renal function,

(iii) iminodiacetate derivatives, especially acetanilido-IDA ligands, pyridoxylidene glutamate and other Schiff bases, 8-hydroxyquinoline derivatives, etc for hepatobiliary function studies,

(iv) pyrophosphate, tetracycline and glucoheptonate for myocardial infarct localization,

(v) ditertiary arsine and phosphine ligands for the imaging of myocardium,

(vi) human serum albumin (HSA) for blood pool imaging and for determination of plasma volumes and fibrinogen and plasmin for clot localization,

(vii) erythrocytes (red blood cells) for blood pool imaging, red cell mass determination, nuclear cardiology, detection of vascular malformations, spleen imaging and detection of gastrointestinal tract bleeding,

(viii) sulphur colloid and phytate for the imaging of the reticuloendothelial system (liver, spleen, bone marrow) and antimony sulphide colloid for lymphoscintigraphy and

(ix) macroaggregates and microspheres of HSA for evaluation of the lung arteriolar capillary bed and for blood perfusion of various organs including the heart.

It is only recently that concerted efforts have begun in order to characterize many of the above agents with respect to their purity, structure, chemical reactivity and various physico-chemical parameters[3].

Chemistry of Technetium

The systematic chemistry of technetium is relatively unexplored although several advances have been made very recently. A number of reviews are available which summarize the existing knowledge on various aspects of the chemistry of this element and their interrelationships with nuclear medicine[7-14]. However, it should be noted that some of the earlier reviews contain incorrect results which no doubt were due to the difficulties inherent in working with small quantities of radioactive materials.

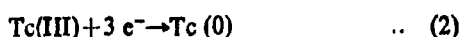
Electrochemistry :

The polarographic behaviour of technetium has been the subject of numerous studies. Techniques employed include classical d.c. polarography as well as a.c. polarography, chronopotentiometry, fast

polarography, pulse polarography and cyclic voltammetry, etc. In addition, allied techniques such as coulometry and amperometry have also been utilized. Despite the fact that most technetium reductions at the dropping mercury electrode are usually irreversible, polarographic techniques have afforded a means of establishing the oxidation states which are stabilized in various media Despite a large early literature on the polarographic reduction of technetium[8], considerable confusion exists as to the exact number of electrons involved in the various reduction processes. The initial 3- or 4-electron reduction waves occur in acidic media at sufficiently positive potentials providing satisfactory data. Results are unreliable in the presence of highly acidic solutions, especially HCl, because of the side reactions due to the dissolution of mercury and subsequent reduction of pertechnetate. The data obtained using hydrochloric acid at a concentration of 0 1 *M* or more as an electrolyte should thus be interpreted with caution Reductions in buffered acidic media take place in multiple steps. A rather well formed first wave occurs for a diffusion controlled four-electron reduction and it shifts with *p*H approximately as follows :

$$E_{\frac{1}{2}} = A - 0\,10\,pH\,(pH\,0-7) \quad \cdots \quad (1)$$

where A is +0 06, +0.05 and +0.12 V for perchloric, hydrochloric and sulphuric acids, respectively. A subsequent wave at −0 9 V corresponds to the three-electron reduction to the metal :

$$Tc(III) + 3\,e^- \rightarrow Tc\,(0) \quad \cdots \quad (2)$$

If the pre-contact of the solution with mercury has not been carefully avoided, the data in hydrochloric and sulphuric acid media often show equal intensity waves I ($4e^-$) and II ($3e^-$). The relative heights, however, are in better agreement in perchloric acid media The half-wave potential for the first wave is not affected significantly by the presence of complexing agents, the rate-determining step being :

$$HTcO_4 + e^- \rightarrow HTcO_4^- \quad \cdots \quad (3)$$

The $HTcO_4^-$ undergoes a rapid sequence of fast reactions to produce technetium(III) Using cyclic voltammetry or anodic-sweep pulse polarography, the technetium(III) can often be reoxidized to technetium(IV) or even technetium(V)[15]. The second wave at −0 9 V gives only an upper limit for *n* (electron change) because of the presence of a catalytic component Further waves occurring at more cathodic potentials are very large and obviously catalytic.

In buffered alkaline media, several waves are also found but the wave heights do not often correspond to integral values of *n*. Several workers have found a rather well defined wave at − 0 8 V regardless of the presence of complexing agents[15]. It was postulated that a one-electron change resulting in the formation of technetate ion, TcO_4^{2-}, an unstable species in water, accounts for the rate-determining step. Non-integral values between 2 and 4 were reported for the total number of electrons transferred The second wave at about− .0 V corresponds to a value of *n* of between 4 and 5. In unbuffered neutral or alkaline media, pertechnetate shows much more complicated behaviour though not too unsimilar to that in buffered alkaline media. It has been proposed that the alkaline environment produced at the electrode surface during pertechnetate reduction accounts for the similarity[15].

Reducing agents :

With the exception of pertechnetate itself, and perhaps technetium-99m-labeled sulphur colloid, all other radiopharmaceuticals contain technetium in an oxidation state lower than seven. Reduction of pertechnetate is thus a prerequisite before achieving successful incorporation of technetium into any of a variety of useful ligands. Pertechnetate itself does not bind to complexing ligands or to any extent with molecules of biomedical interest When injected intravenously, as for brain imaging, pertechnetate becomes weakly bound to albumin, largely through electrostatic interactions. This binding is not strong and pertechnetate thus bound can be easily displaced by anions such as perchlorate. Pertechnetate solutions can be reduced by many common reducing agents. In principle, any reductant with a reduction potential lower than that of pertechnetate (+0.738 V) is capable of performing the reduction. The pertechnetate ion is a mild oxidizing agent (unlike the strongly oxidizing permanganate) and its reduction is generally favoured in a number of media of interest in nuclear medicine The production of the insoluble oxide, TcO_2, or a hydrate thereof, however, is thermodynamically favoured in aqueous solutions except in highly acidic media, or in the presence of complexing agents. Formation of the oxide is a competitive pathway in all reduction reactions and has to be avoided in carrying out the preparation of soluble radiopharmaceuticals Chemistry of the reducing agent also plays a very important role, especially when using metallic reducing agents.

The most frequently used reducing agents include stannous ion, ferric chloride and ascorbic acid, conc. HCl, borohydride and dithionite[8]. Others such as cuprous ion, formamidine sulphinic acid, and sulphhydryl compounds have also been employed. Electrolytic reduction using inert as well as tin or zirconium electrodes can also be employed in some systems. During the preparation of radiopharmaceuticals, reductions are generally carried out in the presence of a complexing ligand (often a compound that one wishes to label with ^{99m}Tc) that stabilizes the lower oxidation state of technetium and thus eliminates or minimizes subsequent hydrolytic reactions. Redox reactions involving pertechnetate most likely proceed via oxygen atom transfer to the reducing agent and are favoured with reductants that react by such a mechanism. The reductions are thermodynamically favoured in general but the kinetic parameters often assume a greater importance. Stannous compounds are employed as

reducing agents in most radiopharmaceutical preparations, despite the various reported problems[16].

Synthetic and Structural Studies

The last few years have experienced an intense surge of interest in the area of synthesis and structure elucidation of technetium coordination compounds. The fact that technetium has one of the most complicated and subtle chemistries compared to other elements used in nuclear medicine applications is not totally without advantage since the intricate chemistry also offers almost unlimited possibilities of manipulation in order to produce a wide range of complexes with tailor-made properties. Certain lower oxidation states of technetium can be stabilized against subsequent ligand substitution by choosing an appropriate coordination environment, which is expected to make the complexes retain their *in vivo* integrity. Accordingly, the areas of intense research effort recently in controlled syntheses of a wide variety of stable, substitution inert technetium complexes and the elucidation of their structure and chemistry promise to substantially add new and useful agents to our existing armamentarium of ^{99m}Tc radiopharmaceuticals. Additionally, a number of model technetium compounds that have been synthesized no doubt will permit a study of the *in vitro* and *in vivo* reaction mechanisms and thus provide a basis for elucidating structure-activity relationships and consequently aid in the development of new or improved agents for various applications in nuclear medicine. This intensified interest is exemplified by the fact that about five years ago, only a handful of simple technetium compounds had been synthesized and characterized. The structure of these compounds was poorly understood. A number of coordination compounds with technetium in oxidation states ranging from 1+ to 7+ and with coordination numbers from 4 to 8 have since been prepared and structurally characterized by definitive techniques such a single crystal X-ray analysis.

1. *Synthesis* :

The predominantly used method so far for preparing technetium–99m radiopharmaceuticals is by the so-called redox route, for example, by the stannous reduction of pertechnetate in the presence of a potential complexing ligand. Despite the limitations involved in this method, it has allowed the development of a variety of extremely useful radiopharmaceuticals Another possible approach is the synthesis of ^{99m}Tc-labeled compounds utilizing ligand substitution reactions, that is by substitution of the desired ligand onto a stable, characterized, prereduced technetium center. This approach is not without disadvantages ; however, several advantages become obvious such as a control over the oxidation state and coordination environment of technetium in the final product, synthetic possibilities with a greater variety of ligands and the possibility of manipulating biological selectivity by retaining some ligands and changing others in a methodical manner. While examples of this having been accomplished at the no-carrier-added level are so far relatively scarce, attempts at carrying out ligand substitution reactions at the carrier technetium level have met with considerable success[8].

For macroscopic amouts, the substitution route for preparing Tc(V) and Tc(IV) complexes is convenient because of the availability of $TcOX_4^-$ and TcX_6^{2-} materials (X=halogen). These reactions are usually conducted in organic solvents such as ethanol or THF in order to prevent disproportionation and hydrolysis of the starting material. Due to the fairly labile nature of the d^2 center, the reactions proceed rapidly to yield five-, six- and seven-coordinate complexes with an intact TcO^{3+} core. Under anhydrous conditions the octahedral d^3 center, however, is substitutionally inert and somewhat forcing conditions are required to drive the reactions to completion. $TcCl_6^{2-}$ reacts more rapidly than TcI_6^{2-} ; in aqueous media these compounds are quite labile and produce the insoluble TcO_2. At the no-carrier-added level, well-defined $TcOX_4^-$ and TcX_6^{2-} species are not generally accessible. There are several poorly defined technetium-99m complexes however, that have been utilized as substrates for substitution syntheses to produce complexes with glucoheptonate, gluconate, DTPA, citrate and cyclam, etc[14].

(i) *Simple salts and complexes with inorganic ligands* : The heptavalent state is normally most stable in simple salts (e.g. TcO_4^-) followed by the tetravalent state (e.g. TcO_2). The other oxidation states generally gain stability via complex formation. The oxides, sulphides and simple oxo-anions have all been well characterized. The weakly paramagnetic, volatile heptoxide has a structure consisting of two TcO_4 tetrahedra which share an oxygen atom in a linear Tc-O-Tc array[14] The black TcO_2 with a distorted rutile structure is formed from reduction of TcO_4^-, by hydrolysis of hexahalogenotechnetate(IV) complexes, or by thermal decomposition of NH_4-$[TcO_4]$ at 950° in a nitrogen atmosphere. Several ternary oxides have also been reported, for example $NaTcO_3$, $M_2^ITcO_3$, Li_2TcO_4, Li_4TcO_5 and $M_2^ITcO_4$, etc.[17]. The sulphides Tc_2S_7 and TcS_2 are isomorphous with the corresponding oxides. The heptasulphide is volatile and can be prepared by addition of H_2S, thioacetamide or thiosulphate to acid solutions of pertechnetate.

Various halides, thiocyanates and oxohalides of technetium are known and have been studied extensively[14]. Most of these compounds are not stable in neutral aqueous media and the synthetic schemes involving these as starting materials are carried out in acidic solutions or in non-aqueous solvents. One of the important intermediates is square-pyramidal $TcOX_4^-$ which is produced upon reduction of TcO_4^- with concentrated halogen acid[18]. Octahedral $[Tc(NCS)_6]^{2-}$ and $[Tc(NCS)_6]^{3-}$ have been prepared by the reaction of $(NH_4)SCN$ with a solution of $(NH_4)_2[TcX_6]$ compounds[19]. All SCN^- ligands are N-bonded and a nearly perfect octahedral symmetry exists for $(Bu_4N)_2[Tc(NCS)_6]$, as demonstrated by X-ray structural studies. Various cyanide

complexes containing the TcO^{3+}, *tr*-TcO_2^+ and *tr*-$Tc(O)(OMe)^{2+}$ cores have recently been prepared and characterized[20]. A variety of carbonyl, nitrosyl and organometallic compounds of technetium have been reported in the early as well as recent literature. Also, a range of mixed-ligand Tc(I) complexes of the type $Tc(CO)_{5-n}L_n$ (L=monodentate organic ligand, e.g. Py, PR_3 or AsR_3) have been synthesized and studied.

(ii) *Coordination complexes containing organic ligands* :

(*a*) *Oxygen donor ligands* : Complexes of technetium that have been prepared and characterized with this class of ligands include β-diketonates, [$TcCl_4$-(sal)], diphosphonates, etc. The neutral complex $Tc(acac)_3$ has recently been obtained by refluxing TcO_4^- in neat acetylacetone[21,22] Earlier, it was prepared by refluxing $TcCl_4(PPh_3)_2$ with the ligand in an analogous reaction[23]. Reaction of (PPh_4)-[TcX_6] or $TcX_4(PPh_3)_2$ (X=Cl, Br) with anhydrous acetylacetone under different conditions also produces mixed ligand Tc(III) and Tc(IV) complexes such as $Tc(acac)_2X_2$. $PPh_4[Tc(acac)X_4]$. $Tc(acac)_2$-PPh_3X, etc.[22,23]. The latter compound displays a *trans* configuration with a coordination polyhedron approximating D_{4h} symmetry based on X-ray structural studies. The reaction of excess methylene diphosphonate (routinely used skeletal imaging agent) with $[TcBr_6]^{2-}$ produces a mixture of species. Purification yields a material that has been shown by X-ray analysis to be polymeric with a Tc/MDP ratio of 1.0[24]. Each Tc center has an octahedral coordination environment. Two symmetry related Tc atoms are bridged by each MDP ligand and each Tc atom is bound to two symmetry related MDP ligands Even though the oxidation state of the Tc center cannot be assigned unambiguously, Tc(IV) or Tc(V) appear to be most likely present. Such structures are also likely with the other commonly used diphosphonate bone agents. The actual radiopharmaceuticals (^{99m}Tc-methylene diphosphonate, ^{99m}Tc-ethylidenehydroxy disodium phosphonate) have recently been shown using HPLC techniques to contain a mixture of species in solution[25]. The individual components all localize in bone but significant differences exist in their blood clearance, soft tissue uptake and excretion from the body.

(b) *Nitrogen donor ligands* : A variety of complexes of technetium with this class of ligands have recently been synthesized and studied. Examples are $[TcO_2(en)_2]X$ (X=Cl, Br, I), $[TcO_2(cyclam)]$-$ClO_4.H_2O$, complexes with 1,2-diaminocyclohexane, 1,2-diaminopropane, several pyridine derivatives, and imidazole, TcO_2XL type compounds (where L=bipy, X=Cl, Br or L=phen, X=Cl), [TcO($HBPz_3$)-Cl_2] [where $HBPz_3$=hydrotris (1-pyrazolyl)borate] and $[Tc(DMG)_3\,SnCl_3(OH)].3H_2O$ (DMG=dimethylglyoxime)[18,14,21,26,27]. Both the ethylenediamine and cyclam complexes contain the *tr*-TcO_2^+ core embedded in an approximately octahedral coordination environment provided by the four nitrogen donor atoms. The Tc=O bond length in both complexes is considerably longer (*ca* 1.75 Å) than the average Tc=O length (*ca* 1 65Å) observed in complexes that contain the TcO^{3+} core The Tc=O ir stretching modes (790 and 834 cm^{-1} for cyclam and en complexes, respectively) are below the range (1020 – 910 cm^{-1}) observed for νTc=O in TcO^{3+} complexes It appears that charge neutralization of the Tc center is one of the factors that governs whether a given Tc(V) complex will contain the TcO^{3+} or the *tr*-TcO_2^+ core. The dimethylglyoxime complex is obtained upon the reduction of TcO_4^- by Sn^{2+} in the presence of the ligand In this compound the tin and technetium are connected by a triple bridge, the separation between metal centers is 3. 7Å[27]. The tin atom can be viewed as "capping" the three oxygen atoms on one end of the Tc-DMG complex. The oxidation states of tin and technetium in this diamagnetic complex have been assigned as IV and V, respectively[27]. Mixed tin-technetium complexes could be present in radiopharmaceuticals that are usually prepared using Sn(II) as a reductant.

(c) *Sulphur donor ligands* : Since sulphur containing ligands are often used in ^{99m}Tc radiopharmaceutical preparations, a number of workers have recently undertaken studies of the interaction of sulphur donor ligands with technetium. A variety of complexes have been prepared and characterized $(Ph_4As)[TcO(dithiolate)_2]$, (Bu_4N)-$[TcO\{SC(O)CH_2S\}_2]$, $[TcO(C_2O_2S_2)_2]^-$, $[TcO\{S_2C_2(CN)_2\}_2]^-$, $[TcO(tdt)_2]^-$ (tdt=3,4-dimercaptotoluene) and $TcN(S_2CNEt_2)_2$, etc[14]. Both dithiolato and thioglycolate materials contain the TcO^{3+} core in a distorted square pyramidal environment and the Tc is displaced about 0 76 Å above the plane of the sulphur atoms. The displacement of halide from $[TcOCl_4]^-$ has led to a systematic synthesis of a large variety of *bis*(dithiolato) technetium(V) complexes mentioned above. All these compounds display square pyramidal geometries and exhibit Tc=O stretches in the ir region at 920–980 cm^{-1} ; complexes that contain electron withdrawing substituents on the ligands exhibit Tc=O stretching frequencies towards the higher end of this range. Analogous square pyramidal complexes containing the O,S chelated ligand rather than the S,S chelated ethanedithiolato ligand have recently been prepared[14] A technetium(V) complex containing the $Tc\equiv N^{2+}$ core has also recently been synthesized and characterized[28] . Hydrazine reduction of TcO_4^- followed by reaction with $Na(S_2CN\,Et_2)$ gives the uncharged nitrido complex $TcN(S_2CNEt_2)_2$. Analogous to the *bis*(dithiolato) TcO^{3+} complexes, the geometry of the nitrido complex is square pyramidal with an axial Tc≡N bond and the Tc atom is 0 75 Å above the plane of the four sulphur atoms This complex is isostructural with ReN-$(S_2CN\,Et_2)$.

(d) *Phosphorus and arsenic donor ligands* : A number of phosphine and arsine complexes have been described ; these all contain (with a few exceptions) technetium in IV or lower oxidation states[14]. This is a reflection of both the reducing action of these ligands as well as the "softness"

of the donor atoms that favour stabilization of lower metal oxidation states. The exceptions involve the Tc(V) center which is stabilized either by the presence of special ligands such as diars or by the presence of oxo ligands, e.g., those that result in the formation of the TcO_2^+ core, and thus decrease the effective formal charge on the central metal atom The octahedral complexes $[Tc(PPh_3)_2Cl_4]$ and $[Tc(AsPh_3)_2Cl_4]$ are produced upon the reaction of PPh_3 or $AsPh_3$ with $(TcCl_4)_n$ in refluxing ethanol. The magnetic moments are respectively 3.92 B.M. and 3.62 B.M. consistent with a Tc(IV) (d^3) species. On the contrary, reaction of 1,2-*bis* (diphenylphosphine)ethane (dppe) under similar conditions gives the Tc(III) complex, *tr*-$[Tc(dppe)_2Cl_2]Cl$. When excess dppe is used, further reduction leads to the formation of Tc(II) complexes, *tr*-$[Tc(dppe)_2X_2]$ (X=Cl, Br) ; these readily oxidize in air to give the Tc(III) analogs. Many of these complexes have been prepared and structurally characterized. Potential use of ^{99m}Tc analogs as heart imaging agents has recently been demonstrated[29]. The synthesis of $[Tc(diars)_2Cl_4]^+$, an eight-coordinate technetium(V) complex by oxidative addition of molecular chlorine to *tr*-$[Tc(diars)_2Cl_2]^+$ was described as early as 1960. The diars ligand has previously been shown to stabilize higher coordination numbers. A variety of other complexes with phosphorus and arsenic donor ligands have been described in the literature[14].

(e) *Mixed donor atom ligands* : Several technetium complexes with N,O chelating Schiff bases and aminepolycarboxylate ligands and with other mixed donor atom ligands have been prepared and studied[14]. The compounds include $[TcO(Ph\text{-}sal)_2Cl]$ and $[TcO(Ph\text{-}sal)Cl_2]^-$ (Ph-salH=N-phenylsalicylideneimine) ; $(H_2EDTA)Tc(u\text{-}o)_2Tc(H_2EDTA)\text{-}5H_2O$, $Ba[Tc(O)EDTA]_2$, $[Tc_2(OC_5H_4N)_4]_n^{n+}$ and $(Ph_4As[TcOL_2]$ where L=R CH(S)COO⁻. In case of the Tc(V) Ph-salH complex, an octahedral structure was suggested in which a phenolic oxygen atom was situated *trans* to the Tc=O bond. The EDTA ligand, depending on reaction conditions forms several different complexes. For example, a strong Tc-Tc bond with a short 2 33 Å distance has been shown to be present in $(H_2EDTA)Tc(u\text{-}o)_2Tc(H_2EDTA).5H_2O$ and each EDTA coordinates to one technetium by two nitrogen and two oxygen atoms[30]. Each technetium has an octahedral geometry and perhaps a 4+ oxidation state. Reaction of H_4EDTA with $[TcOCl_4]^-$ in anhydrous DMSO gives $[Tc(O)EDTA]_2^{2-}$, the barium salt of which contains two $[Tc(O)EDTA]^-$ anions, each coordinated to barium ions via four carboxylate bridges[14]. The barium is thus eight-coordinate and each technetium atom is seven-coordinate with a distorted pentagonal bipyramidal geometry and the EDTA ligand is hexadentate. This complex illustrates the structural flexibility of the d^2 TcO^{3+} core, which has recently been observed to occur in technetium complexes with 5, 6 and 7 coordination numbers.

2. *Structural studies :*

Various techniques that have been used for the structure elucidation of technetium compounds include X-ray analysis, elemental analysis and molecular weight determination, ir, Raman, nmr and vis/uv spectroscopy and mass spectroscopy. Definitive structures have been assigned to approximately 65 compounds using X-ray structural analysis[31]. A partial listing of these appears in Table 1. These

TABLE 1—TECHNETIUM COMPOUNDS STRUCTURALLY CHARACTERISED BY SINGLE CRYSTAL X-RAY ANALYSIS[8,14,31]

Compound*	Oxidation state of technetium	Coordination number
$K_5Tc(CN)6$	I	6
$[trans\text{-}Tc(NH_3)_4(NO)(H_2O)]^{2+}$	I	6
$TPP[Tc(CO)_3]_2$	I	6
$TcCl_2[(EtO)_2PPh]_4$	II	6
$Tc(diphos)_2Cl_2$	II	6
$[Tc(NO)Br_4]^-$	II	5
$[Tc_2Cl_8]^{3-}$	II, III	6
$TcCl_3(CO)(Me_2PPh)_3 . EtOH$	III	7
$[Tc(diars)_2Cl_2]^+$	III	6
$TcCl_3(Me_2PPh)_3$	III	6
$TcCl(acac)_2(PPh_3)$	III	6
$Tc_2[OOCC\ Me_3]_4Cl_2$	III	6
$[Tc(dmpe)_2Cl_2]^+$	III	6
$[Tc(diphos)_2X_2]^+$, X=Cl or Br	III	6
$[Tc(SCN)_6]^{3-}$	III	6
TcO_2	IV	6
$[TcCl_6]^{2-}$	IV	6
$[TcOCl_4]^-$	V	5
tr-$[TcO_2(en)_2]^+$	V	6
tr-$[TcO_2(Cyclam)]^+$	V	6
$[TcO(EDTA)]^-$	V	7
$[TcO(SCH_2CH_2S)_2]^-$	V	5
$[TcO\{SCH_2C(O)S\}_2]^-$	V	5
$[TcO(SCH_2CH_2O)_2]^-$	V	5
$[Tc(diars)_2Cl_4]^+$	V	8
$[TcO(HBPz_3)Cl_2]$	V	6
$Tc(dmg)_3(SnCl_3)(OH) . 3H_2O$	V	7
$[TcOF_4]_3$	VI	6
$(Me_4N)_2[TcO_4]$	VI	4
Tc_2O_7	VII	4
Tc_2S_7	VII	4
$Li_5[TcO_6]$	VII	4
$Na_3[TcO_5]$	VII	4
$[Tc(OH)(MDP)^-]_n$	?	6

*Abbreviations TPP, tetraphenylporphine , diphos, *bis*-(1,2-diphenylphosphino)ethane ; diars, *o*-phenylene*bis*-(dimethylarsine) , acac, acetylacetonate monoanion ; dmpe, *bis*-(1,2-dimethylphosphino)ethane ; en, ethylenediamine ; cyclam, 1,4,8,11-tetrazacyclotetradecane ; EDTA, ethylenediaminetetraacetate , $HBPz_3$, hydro*tris*-(1-pyrazolyl)borate monoanion , dmg, dimethylglyoxime in unknown protonation state , MDP, methylene diphosphonate in unknown protonation state ; Me, methyl , Et, ethyl , Ph, phenyl

studies provide several results of considerable importance to the design and development of technetium radiopharmaceuticals : (i) A wide range of coordination numbers and geometries is exhibited by complexes of reduced technetium. Even though 6-coordination with an octahedral geometry is most common, the compounds are not restricted to only such structures as generally assumed in the early literature In simple compounds, a coordination number of four is limited to the 7+ state in the

per salts and the oxide halides; 6-coordination can be assumed by most other lower oxidation states. Five-coordinate compounds with square pyramidal geometry and 7-coordinate compounds with a geometry approximating that of a monocapped octahedron are quite often encountered. (ii) The 5+ oxidation state is more common than previously assumed, when the complexes are prepared using aqueous and aerobic conditions (iii) A number of complexes contain the Tc(V)=O center such as in $TcOCl_4^-$ and in others. and often bridging oxygen atoms. The likely conclusion is that many technetium radiopharmaceuticals prepared by the reduction of pertechnetate in aqueous media may indeed contain one or two oxo ligands and the properties associated with the chemistry of such linkages The oxo group in Tc=O compounds exerts a strong *trans*-labilizing effect with the result that the *trans* coordination site is vacant in compounds such as $TcO(SCH_2CH_2S)^{2-}$, $TcO[SCH_2C(O)S]^{2-}$ $TcOCl_4^-$ etc., or is loosely occupied by a solvent molecule when the compounds are in solution. In $Tc(HBPz_3)Cl_2O$, five coordination is not favoured due to the tridentate nature of the $HBPz_3^-$ ligand but the influence of the oxo group leads to a weak *trans* ligand-metal bond as reflected by the *trans* nitrogen atom being 0.2 Å further from technetium than are the two *cis* nitrogen atoms[14]. The four equatorial coordination sites *cis* to the oxo ligand are resistant to ligand substitution (in contrast to the labile *trans* site) and thus such structures should provide suitable templates about which to construct radiopharmaceuticals with maximum *in vivo* integrity. The occurrence of tightly bonded Tc(V)=O centers and the different bonding properties of the equatorial and axial sites within these centers may be more commonly involved in routine ^{99m}Tc radiopharmaceuticals than generally recognized. (iv) Technetium can form complexes with metal-metal bonds as exemplified by the structures of $Tc_2Cl_8^{3-}$ and $Tc_2[OOCC(Me)_3]_4Cl_2$ and this possibility should not be overlooked in the assignment of possible structures. (v) Analogous to the well known nitrosyl-ruthenium complexes, *trans*-$Tc(NH_3)_4(NO)(OH_2)^{2+}$ could represent a large class of nitrosyl-technetium complexes. By virtue of the fact that the NO ligand stabilizes low oxidation states, compounds with Tc-NO centers should be an interesting class to be exploited.

The solid state structure of $[Tc(OH)MDP^-]_n$ (and perhaps other bone agent complexes such as pyrophosphate, polyphosphate etc.) shows the compound to be polymeric with technetium centers bridged by MDP and OH (or OH_2) ligands, and MDP ligands in turn bridged by technetium centers. This would indicate that technetium phosphate radiopharmaceuticals may be polymeric mixtures in aqueous solution and not single well defined species. Ligands such as EDTA and DTPA are capable of forming dimeric metal complexes and can also simultaneously coordinate to more than one metal. With the use of tin(II) as a reducing agent in radiopharmaceutical formulations, the possibility of mixed technetium-tin-ligand complexes cannot be ruled out completely.

Conclusion

Technetium has played a vital role in the rapidly growing field of diagnostic nuclear medicine. A plethora of ^{99m}Tc-labeled compounds is already available for various imaging applications, many others continue to be developed at a rapid pace. The lack of a proper understanding of the exact nature of most earlier technetium radiopharmaceuticals and their mode of action did not significantly hamper the practical usefulness of this radionuclide in diagnostic applications. The ultimate benefits to the patients have been immeasurable. Recently, however, a growing awareness of the need to systematically understand the chemistry and *in vivo* reaction mechanisms of technetium radiopharmaceuticals has resulted in a flurry of research activity in this area The last five years have seen many important advances including those in the field of technetium coordination chemistry, and in the application of highly sensitive analytical techniques to the fractionation and characterization of complex technetium radiopharmaceutical mixtures. The knowledge that has been acquired will certainly add new and more efficacious ^{99m}Tc radiopharmaceuticals to our existing arsenal and will also result in improvement of the existing agents. Many of the technetium labeled compounds developed earlier included particles and a prior understanding of factors such as the chemical state of technetium and various thermodynamic and kinetic parameters etc. were not crucial to the usefulness of these agents for the intended application. In contrast, effective development and use of many biological compounds and drug molecules labeled with technetium require a thorough understanding of the chemistry, the binding affinities and the effect of the metal on the biological properties of the substrate. Direct binding of technetium to bioactive molecules may be of limited usefulness since in most cases biological behaviour of the labeled compound is drastically altered. In this respect, some of the more recent approaches such as binding technetium to a chelate containing derivative of a biologically active molecule may be of particular value. Work in this direction is already underway and some success has been demonstrated. The major stumbling block has been the synthesis of derivatives of the parent molecule with retention of biological activity.

Recent renewed interest in the area of synthetic and structural coordination chemistry of technetium will undoubtedly play a very important role in the development of improved radioscintigraphic agents. It will be necessary to understand the chemical mechanisms involved in many of these synthetic reactions especially with regard to ligand substitution and oxygen atom transfer redox processes. Such mechanistic studies will complement the large body of knowledge that has slowly been evolving on the synthetic and structural aspects of technetium chemistry.

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Mass Spectrometry of Transition Metal π-Complexes. Part—VII. A Study of the Behaviour of Some Ruthenocene Derivatives[†]

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The mass spectral fragmentation of $(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_5H_4COR)$ (R = CH_3, Ph) (I, II) and $(\eta\text{-}C_5H_4COCH_3)Ru(\eta\text{-}C_5H_4COCH_3)$ (III) has been examined and compared with that of the ferrocene analogues. The higher metal-ligand bond strengths in the ruthenocene derivatives are reflected in much more extensive fragmentation of the metal-bound ligands compared to the behaviour of the ferrocenes The ion, $(M\text{-}CH_3)^+$ from (III) shows an unusual loss of two CO groups in a single step, a process believed to be under thermodynamic control and leading to $[(C_5H_5)Ru(C_6H_6)]$.

THE mass spectral behaviour of ferrocene derivatives has been the subject of extensive study and much of this work has been reviewed[1]. However, there has been no such studies on the ruthenocene analogues and only three studies have been reported on ruthenocene itself[2,3,4]. Of particular interest is the study of Müller and D'Or[3] which showed that 8.3% of the total metal-containing ion current of ruthenocene consists of ions of the type $MC_8H_x^+$ and $MC_6H_x^+$, arising via successive loss of C_2 units from the molecular ion, compared to 1.1% for ferrocene. Furthermore, 9.5% of total metal-containing ion current of ruthenocene consists of ions of the type $MC_4H_x^+$, $MC_3H_x^+$, $MC_2H_x^+$ and MCH_x^+, arising principally by fragmentation of $MC_5H_5^+$, compared to 6.2% for ferrocene. The percentages of $(Metal)^+$ are 13 3% for ferrocene and 1.8% for ruthenocene. These small, but significant, differences are in accord with slightly higher $M\text{-}C_5H_5$ bond dissociation energies in the ruthenium compound[1,3,4]. We were interested to see if these differences would also manifest themselves in the mass spectra of substituted ruthenocenes and report here the behaviour of monoacetyl- and monobenzoylruthenocene (I and II) and 1.1'-diacetylruthenocene (III).

Results and Discussion

The spectrum of I is listed in Table 1 and is to be compared with that of monoacetylferrocene (IV) which has been previously reported[5], but which was redetermined in this work (Table 2). Metastable peaks confirm only four fragmentations in IV. These are $M^{+\cdot} \rightarrow [M\text{-}CH_3]^+$, $[M\text{-}CH_3]^+ \rightarrow [M\text{-}CH_3CO]^+$, $M^{+\cdot} \rightarrow [M\text{-}CH_3CO]^+$ and $[(C_5H_4)Fe(C_5H_5)]^+ \rightarrow [C_5H_4.C_5H_5]^+$. The fragmentation of I (Table 1) is supported by only two metastable peaks which confirm the first two of these fragmentations.

Two additional fragmentations of the molecular ion of I are observed over those of IV. These are loss of CH_2CO yielding $[(C_5H_5)Ru(C_5H_5)]^{+\cdot}$ and

TABLE 1—MASS SPECTRUM OF MONOACETYLRUTHENOCENE (I)

m/z⁺	Rel Abd (%)	I/ΣI (%)*	Assignment
274	100	42	$(C_5H_5)Ru(C_5H_4COCH_3)^{+\cdot}$
254	21	9	$(C_5H_5)Ru(C_5H_4CO)^+$
245	1 5	1	$C_5H_5Ru(C_6H_6)^+$
232	5	2	$(C_5H_5)Ru(C_5H_5)^+$
231	32	14	$(C_5H_5)Ru(C_5H_4)^+$
205	14	6	$(C_5H_5)Ru(C_3H_2)^+$
191	1	0 5	$(C_5H_4)Ru(C_2H)^+$
180	1	0.5	$Ru(C_6H_6)^{+\cdot}$
179	4	2	$Ru(C_6H_5)^+$
167	16	7	$Ru(C_5H_5)^+$
154	4	2	$Ru(C_4H_4)^{+\cdot}$
153	1	0.5	$Ru(C_4H_3)^+$
141	6	2.5	$Ru(C_3H_3)^+$
140	5	2	$Ru(C_3H_2)^{+\cdot}$
139	7	3	$Ru(C_3H)^+$
130	1	0 5	$Ru(C_2H_4)^{+\cdot}$
129	2	1	$Ru(C_2H_3)^+$
128	1	0.5	$Ru(C_2H_2)^{+\cdot}$
127	1	0 5	$Ru(C_2H)^+$
114	8	4	$RuC^{+\cdot}$
102	4	2	$Ru^{+\cdot}$
92	2		$C_5H_4CO^+$
78	0.7		$C_6H_6^{+\cdot}$
77	1		$C_6H_5^+$
65	1.5		$C_5H_5^+$
64	2		$C_5H_4^{+\cdot}$
63	3		$C_5H_3^+$
52	1		$C_4H_4^+$
51	1.5		$C_4H_3^+$
50	1		$C_4H_2^{+\cdot}$
43	14		CH_3CO^+
39	7		$C_3H_3^+$

Metastable ions m/z 244.8 274 → 259
m/z 206.0 259 → 231

⁺ Based on ^{102}Ru

* Metal-containing ions only. All percentages rounded to the nearest 0.5%.

Dedicated to Professor A K. Dey on the occasion of his 60th Birthday

† Part VI, R. Davis, M. L. Webb, D. E. Millington and V. Parr, *Org. Mass Spectrom.*, 1979, 14, 289.

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TABLE 2—MASS SPECTRUM OF MONOACETYLFERROCENE (IV)

m/z	Rel. Abd. (%)	I/ΣI(%)*	Assignment
228	100	20	$(C_5H_5)Fe(C_5H_4COCH_3)^+$
213	17	3	$(C_5H_5)Fe(C_5H_4CO)^+$
185	83	17	$(C_5H_5)Fe(C_5H_4)^+$
163	14	3	$Fe(C_5H_4COCH_3)^+$
129	77	15	$(C_5H_5\ C_5H_4)^+$
121	60	12	$Fe(C_5H_5)^+$
95	13	3	$Fe(C_3H_3)^{+\cdot}$
94	19	4	$Fe(C_3H_2)^+$
81	21	4	$Fe(C_2H)^{+\cdot}$
71	25	5	$Fe(CH_3)^+$
56	69	14	Fe^+
43	13	–	CH_3CO^+
39	16	–	C_3H_3

* Metal-containing ions only

Metastable ions m/z 199 0 228 → 213
m/z 160 7 213 → 185
m/z 150 1 228 → 185
m/z 90 0 185 → 129

the unusual, although weak, loss of HCO. The product of this later reaction can be written in a number of ways, of which we chose $[(C_5H_5)$-$Ru(C_6H_6)]^+$, despite the fact that this involves a massive reorganisation of the ligand. We are encouraged to do this by the observation of the ions $[Ru(C_6H_6)]^{+\cdot}$, $[Ru(C_6H_5)]^+$, $[C_6H_6]^+$ and $[C_6H_5]^+$ as well as other expected fragments from these ions.

As with ruthenocene, the increase in metal-ligand bond strength in I over IV leads to 77% of metal-containing ions in the former containing greater than five carbon atoms, compared to 40% in IV. 23% of the metal containing ions in I contain five or less carbon atoms compared to 46% in IV and the $(Metal)^{+\cdot}$ ion accounts for 2% of this ion current in I, but 14% in IV.

A number of other differences are noteworthy. Firstly, while IV shows formation of both $[(C_5H_5)Fe]^+$ and $[(C_5H_4COCH_3)Fe]^+$, only the former is observed for I suggesting that the difference between the metal-ligand bond strengths in I is much greater than that in IV. IV also shows a prominent fragmentation, $[(C_5H_5)Fe(C_5H_4)]^+ \rightarrow [C_5H_5\ C_5H_4]^+ + Fe$ which is completely absent in I. Furthermore, no CH_3-transfer to the metal appears to occur in I although this is observed for IV. The ion $[RuC]^{+\cdot}$ is observed and although there is no metastable ion to confirm its genesis, fragmentation of $[Ru(C_3H_2)]^{+\cdot}$ by loss of C_2H_2 would seem an obvious route. Other steps involving C_2H_2 loss are common in the spectrum of I.

A comparison of the behaviour of II and monobenzoylferrocene (V) shows a similar pattern to that established for the monoacetyl derivatives. The fragmentation of V has been reported by others[5] and is similar to that of IV except that the ion $[(C_5H_5)Fe(C_6H_5)]^{+\cdot}$ formed by loss of $C_5H_4CO^{\cdot}$ is the most intense metal-containing fragment ion. In the case of the ruthenocene derivative (Table 3), the fragmentations $M^{+\cdot} \rightarrow (M\text{-}CO)^{+\cdot}$, $M^{+\cdot} \rightarrow (M\text{-}C_6H_5)^+$ and $M^{+\cdot} \rightarrow (M\text{-}C_5H_4CO)^{+\cdot}$ are supported by metastable peaks. As observed above, II also forms the ion $[Ru(C_6H_6)]^+$ but not $[Ru(C_5H_4COC_6H_5)]^+$. Fragment ions formed by phenyl transfer to the metal atom $[(C_5H_5)Ru(C_5H_4)(C_6H_5)]^+$ and $[(C_5H_5)$-$Ru(C_6H_5)]^+$ are observed.

TABLE 3—MASS SPECTRUM OF MONOBENZOYLRUTHENOCENE (II)

m/z⁺	Rel Abd. (%)	I/ΣI(Mo)*	Assignment
336	100	33	$(C_5H_5)Ru(C_5H_4COPh)^{+\cdot}$
308	18	6	$(C_5H_5)Ru(C_5H_4)Ph^{+\cdot}$
306	17	6	$(C_5H_4)Ru(C_{11}H_7)^+$
259	24	8	$(C_5H_5Ru(C_5H_4CO)^+$
244	20	7	$(C_5H_5)RuPh^+$
231	24	8	$(C_5H_5)Ru(C_5H_4)^+$
205	12	4	$(C_5H_5)Ru(C_3H_2)^+$
203	17	6	$(C_5H_5)Ru(C_3H)^+$
167	18	6	$(C_5H_5)Ru^+$
154	7	2	$(C_4H_4)Ru^{+\cdot}$
141	18	6	$(C_3H_3)Ru^{+\cdot}$
139	20	7	$(C_3H)Ru^+$
105	21		$C_6H_5PhCO^+$
102	8	3	Ru^+
77	42		$C_6H_5^+$
65	17		$C_5H_5^+$
64	16		$C_5H_4^{+\cdot}$
63	25		$C_5H_3^+$
51	42		$C_4H_3^+$
50	29		$C_4H_2^+$
39	33		$C_3H_3^+$

Metastable ions m/z 282 3 336 → 308
m/z 199 6 336 → 259
m/z 177 2 336 → 244

⁺ Based on ^{102}Ru

* Metal-containing ions only All percentages rounded to the nearest 1 0 %

71% of total metal-containing ion current of II contains more than five of the ten original cyclopentadienyl carbon atoms and 28% contain five or less carbon atoms. These figures are similar to those observed for I, but not dissimilar to those of V (73% and 27%, respectively). However, only 3% of metal-containing ion current consists of $Ru^{+\cdot}$ ions in II, whereas 13% of that of V consists of $Fe^{+\cdot}$.

The mass spectrum of 1,1'-diacetylferrocene (VI) has also been examined in detail previously[6]. The main decomposition routes of the molecular ion, as evidenced by the observed metastable ions are $M^+ \rightarrow (M\text{-}CH_3)^+$, $M^{+\cdot} \rightarrow (M\text{-}CH_3CO)^+$, $(M\text{-}CH_3)^+ \rightarrow (M\text{-}CH_3\text{-}2CO)^+$ and $(M\text{-}CH_3CO)^+ \rightarrow (M\text{-}CH_3\text{-}2CO)^+$ of which the loss of two CO groups in a single step is the most unusual. This behaviour has been observed in the fragmentation of some metal carbonyl complexes[7]. However, it is without precedent in the fragmentation of organic ketones, although it has been observed in the case of some ketone dimers[8].

In the case of III, metastable ions confirm the fragmentation route, $M^+ \rightarrow (M\text{-}CH_3)^+ \rightarrow (M\text{-}CH_3\text{-}2CO)^+ \rightarrow [M(C_5H_5)]^+$. Thus the single step loss of two CO groups occurs with this molecule also. We propose that the driving force for this unusual fragmentation is formation of $[(C_5H_5)Ru(C_6H_6)]^+$ which must again involve a massive reorganisation of the organic ligands, but which is under thermodynamic control. The other fragmentations of III are all of low abundance (Table 4) and are broadly

in accord with those observed for I. Again, 75% of the total metal-containing ion current contains greater than five cyclopentadienyl ring carbon atoms and 25% contain five or less. The figures for VI are 62% and 38%, respectively.

TABLE 4—MASS SPECTRUM OF 1,1-DIACETYLRUTHENOCENE (III)

m/z⁺	Rel. Abd (%)	I/ΣI (%)*	Assignment
316	90	19	$(C_5H_4COCH_3)Ru(C_5H_4COCH_3)^{+\cdot}$
301	55	12	$(C_5H_4COCH_3)Ru(C_5H_4CO)$
274	5	1	$(C_5H_4COCH_3)Ru(C_5H_5)^+$
259	4	1	$(C_5H_4CO)Ru(C_5H_5)^+$
245	100	21	$(C_5H_5)Ru(C_6H_6)^+$
231	8	2	$(C_5H_5)Ru(C_5H_4)^+$
229	9	2	$(C_5H_5)Ru(C_5H_2)^+$
217	8	2	$(C_5H_5)Ru(C_4H_2)^+$
205	10	2	$(C_5H_4)Ru(C_3H_3)^+$
204	10	2	$(C_5H_4)Ru(C_3H)^{+\cdot}$
191	8	2	$(C_5H_4)Ru(C_2H)^+$
180	15	3	$Ru(C_6H_6)^{+\cdot}$
179	16	3	$Ru(C_6H_5)^+$
178	15	3	$Ru(C_6H_4)^{+\cdot}$
167	50	11	$Ru(C_5H_5)^+$
154	8	2	$Ru(C_4H_4)^{+\cdot}$
153	7	2	$Ru(C_4H_3)^+$
139	9	2	$Ru(C_3H_3)^+$
137	11	2	$Ru(C_3H)^+$
114	14	3	$RuC^{+\cdot}$
102	12	2	$Ru^{+\cdot}$
78	5		$C_6H_6^{+\cdot}$
77	3		$C_6H_5^+$
65	7		$C_5H_5^+$
64	9		$C_5H_4^{+\cdot}$
63	13		$C_5H_3^+$
43	65		CH_3CO^+
39	14		$C_3H_3^+$

Metastable ions m/z 286 7 316 → 301
199.4 301 → 245
113 8 245 → 167

⁺ Based on ^{102}Ru

* Metal-containing ions only. All percentages rounded to nearest 1 0 %.

Thus, in summary, this preliminary study has demonstrated the rich variety of mass spectral fragmentations observed in the spectra of ruthenocene derivatives and further work is in progress in an effort to systematise this behaviour.

Experimental

Ruthenocene was prepared by the method of Pertici *et al*[9]. Mono- and diacetylruthenocene are prepared by the method of Hofler and Schlögl[10]. Monobenzoylruthenocene was prepared by a method exactly analogous to that of the mono-acetyl derivative. All gave satisfactory analytical data, nmr and infrared spectra.

Mass spectra were recorded on an AEI M.S.9. operating at 7 eV and 100 μA trap current and a source temperature of 50°.

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Molecular Orbital Study of $[BFe(CO)_3]^+$, B=(C_5H_5), (C_6H_7) and (C_7H_9)

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SCCC and CNDO calculations are reported for the title series of cations and trends are noted and compared with experimental results The staggered conformation of tricarbonyl [(1,2,3,4,5-η)-2,4-cycloheptadien-1-yl] iron(1+) is shown to be the most stable with a barrier to rotation of 1 8 eV The deformations of (C_7H_9) and (C_6H_7) in the cations are considered. Using the SCCC method, the plane of the saturated carbons is 45° above the plane of the other carbon atoms in $[(C_7H_9)Fe(CO)_3]^+$, while the CNDO value is 42° For $[(C_6H_7)Fe(CO)_3]^+$ the corresponding angles are 50° (SCCC) and 51° (CNDO)

MOLECULAR orbital calculations have been useful in studying trends within a series of related molecules Thus the series $AM(CO)_3$ [AM=(C_6H_6)Cr. (C_5H_5)Mn (C_4H_4)Fe, (C_5H_5)Co and (C_3H_4)Ni] has been studied by the SCCC method considering π orbitals only in the hydrocarbon moiety[1], considering σ and π orbitals[2] and using the CNDO method[3]. In the series $[BFe(CO)_3]^+$, B=(C_5H_5), (C_6H_7), nucleophilic substitution has been correlated with the frontier electron density using the SCCC approach[4]. Using the INDO method, a correlation between the bond indices and the site of nucleophilic addition has been noted for tricarbonyl [(1,2,3 4,5-η)-2,4-cyclohexadien-1-yl] iron (1+)[5]. The bonding in this cation has also been discussed by Hoffmann and Hofmann[6] In the calculations now reported the SCCC method, as used previously, was employed[2]. The experimental geometry of $[(C_5H_5)Fe(CO)_3]^+$ was considered[7]. The structure of $[(C_6H_7)Fe(CO)_3]^+$ was based on the analogous Mn compound[8] and the geometry of hexacarbonyl(transazulene)dimanganese[9] was modified to give the geometry of $[(C_7H_9)Fe(CO)_3]^+$.

The moiety $Fe(CO)_3$ is considered to bond to a hydrocarbon by accepting electrons into the d_{xz} and d_{yz} orbitals of iron and donating them from the $d_{x^2-y^2}$ and d_{xy} orbitals[10-14]. Experimentally it is found that $Fe(CO)_3$ is a net electron donor. For example, by comparing the apparent pK_a values of para substituted anilines it was shown that $Fe(CO)_3$ has an electron donating capacity similar to phenyl[15]. Also coordination with $Fe(CO)_3$ increases the pK_a values of acids confirming the electron donating properties of tricarbonyliron[10,16]. The aromatic nature of $(C_4H_4)Fe(CO)_3$, its ability to undergo electrophilic substitution, supports the electron donating ability of $Fe(CO)_3$[17], as does the increase in stability of carbonium ions following the introduction of tricarbonyliron[18]. From the charges reported in Table 1, it is seen that $Fe(CO)_3$, in all cases, donates electrons to B^+. This is particularly evident from the CNDO results where the hydrocarbon moieties are negatively charged. It may be noted that q_B increases across the series for both the SCCC and CNDO calculations and $q_{(CO)_3}$ decreases using both methods. However q_{Fe} increases using the SCCC method and decreases using the CNDO method across the series though the percentage differences for the iron charges are the smallest. The variations in charge distributions correlate with the carbonyl frequencies as these decrease slightly across the series. Thus in $[(C_5H_5)Fe(CO)_3]^+$ the donation of electrons from iron to B^+ is more significant than the donation to the carbonyls, relative to the later members of the series. Thus low positive charge on B and high positive charges on the carbonyl correspond to high frequencies. The metal in this model does not vary so much in charge. Therefore the model is adequate to interpret the carbonyl frequencies. In the $[BFe(CO)_3]^+$ series, the average charges on B, Fe and $-(CO)_3$ are 0.3, 0 6 and 0.1 and for the $AM(CO)_3$ the corresponding values are -0.1, 0.4

TABLE 1—CHARGES, NORMALISED MULLIKEN POPULATIONS, NORMALISED WIBERG INDICES AND CARBONYL STRETCHING FREQUENCIES

		$[(C_5H_5)Fe-(CO)_3]^+$	$[(C_6H_7)Fe-(CO)_3]^+$	$[(C_7H_9)Fe-(CO)_3]^+$
SCCC	q_B	0 272	0.314	0.325
	q_{Fe}	0.595	0 613	0 627
	$q_{(CO)_3}$	0.113	0.073	0 048
M. P.	M-C(O)	1	0.963	0.885
	C-O	1	1 001	0 996
CNDO	q_B	−0.153	−0 107	−0.055
	q_{Fe}	0 752	0 724	0 704
	$q_{(CO)_3}$	0.401	0.383	0.351
WI	M-C(O)	1	0 982	0 967
	C-O	1	0.997	0 989
ν(CO)[a]		2126	2116	2116
		2078	2066	2062
			1970	1970

[a] Values of F. M Hussein in cm^{-1} measured in acetonitrile.

and -0.3. In the latter case, more electrons are donated to the carbonyls, corresponding to the lower frequencies in this $AM(CO)_3$ series. It is interesting to note that in the CNDO study of $AM(CO)_3$ maximum donation to A occurred in $(C_4H_4)Fe(CO)_3$. Qualitatively by considering LUMO energies, Pettit and coworkers noted that pentadienyl type complexes with $Fe(CO)_3$ have higher frequencies predicted than other complexes with butadiene or non-conjugated dienes[18].

For comparative purposes as both Mulliken population analyses and Wiberg indices are used, these values in the table were normalised to unity for $[(C_5H_5)Fe(CO)_3]^+$. For the C-O values, in general, there is a decrease across the series, with the exception that there is a slight increase in going from $[(C_6H_8)Fe(CO)_3]^+$ to $[(C_6H_7)Fe(CO)_3]^+$ using the SCCC method. However the M-C values do not increase across the series. This is in contrast to the $AM(CO)_3$ series, where the M-C overlap populations decrease using both the SCCC $(\sigma+\pi)$[8] and SCCC (π)[2] methods, while the C-O experimental frequencies and corresponding overlap populations increase across the series. Also the M-C(O) Wiberg indices, in general, decrease and the C-O values increase across the $AM(CO)_3$ series[8]. The field absorption mass spectra of $[(C_6H_7)Fe(CO)_3]^+$ and $[(C_7H_9)Fe(CO)_3]^+$ have been reported and ions corresponding to the loss of one CO from the molecular ions were detected; the spectrum of tricarbonyl(benzene)-chromium consists of only the molecular ion[19]. These results agree with the more negative carbonyl charge in $(C_6H_6)Cr(CO)_3$ and its lower carbonyl frequencies.

In the figure the eclipsed and staggered conformers of $[(C_7H_9)Fe(CO)_3]^+$ are defined, together with the angle α. This angle was varied and it was found, using the SCCC method, that the preferred geometry was the staggered one ($\alpha=0°$), in which there is a CO group below the midpoint of the saturated C-C bond in the hydrocarbon moiety. This result is in agreement with the experimental geometry[9]. The calculated difference between the two conformers is 1 8 eV If one or more CO groups were replaced by larger groups it might be possible to observe the rotamers of such a molecule. A variable temperature ^{13}C nmr study of $(C_7H_9)Fe(CO)_2(CO_2Et)$ showed some evidence for such rotamers by a broadening of the carbonyl shift as the temperature was lowered[10]. Also ^{31}P nmr studies detected rotamers of $[BFe(CO)_{3-x}(EPTP)_x]^+$, $B=(C_6H_7)$, (C_7H_9); x= 1, 2; EPTP=4-ethyl-1-phospha-2,6,7-trioxabicyclo-[2.2 2.] octane[11].

Deformations of the (C_7H_9) and (C_6H_7) ligands may be discussed. The $(C_7H_9)^+$ ligand is predicted on symmetry grounds to be bent rather than planar by considering this ligand as formed from $C_5H_5^+$ and C_2H_4. In the planar geometry, if the π orbitals of ethylene are in the plane of the pentadienyl carbons, there is no interaction. If all the π orbitals are parallel, the hydrogen atoms in $C_5H_5^+$ and C_2H_4 would be sterically unsuitable. In the non-planar case the pentadienyl orbitals in increasing energy
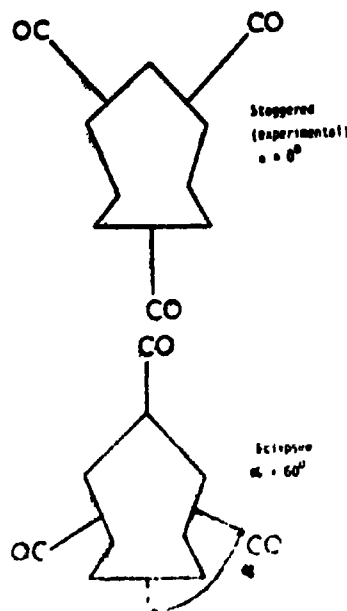
Fig. 1. Staggered and eclipsed conformations of $[(C_7H_9)$-$Fe(CO)_3]^+$.

have symmetries S, A, S, A, S. In $C_5H_5^+$ the lowest two are occupied. Thus the ethylene π(S) can interact with the S LUMO of $C_5H_5^+$ and the A HOMO of $C_5H_5^+$ can also interact with the π^*(A) of ethylene. The sum of the one electron energies of the$[(C_7H_9)$-$Fe(CO)_3]^+$ cation was calculated by the SCCC method for different values of the angle between the C_5H_5 plane and the plane of the saturated carbon atoms of the $(C_7H_9)^+$ ligand. The minimum energy, calculated by aleast squares fit, was at 49° while the experimental value is 39°. The calculations were repeated using the CNDO method and the minimum energy was at 42°, which is closer to the experimental value. Calculations by both the SCCC and CNDO methods confirm the non-planarity of (C_6H_7) in $[(C_6H_7)Fe(CO)_3]^+$. The deformation angle was calculated to be 50° using the SCCC method and 51° using the CNDO approach, while the experimental angle is 43°[9]. Thus, both the SCCC and CNDO methods predict that the deformation in $[(C_6H_7)Fe(CO)_3]^+$ is greater than in $[(C_7H_9)Fe(CO)_3]^+$, in agreement with experiment.

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NMR Spectroscopy of Oriented Organoselenium Compounds

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The use of nmr spectroscopy of oriented molecules in the determination of molecular structure and conformation of organoselenium compounds is presented. Determination of various spectral parameters including their anisotropic contributions is discussed. An up-to-date available information on the selenium compounds is included.

EXTENSIVE use of nmr spectroscopy of molecules oriented in liquid crystals has been made towards the determination of structure and conformation of small organic molecules[1-5]. To a much lesser extent, biologically important systems[6] and inorganic compounds[7] have been investigated using this method, probably due to structural complexities and relatively poor solubilities. On the other hand, the technique promises to provide such structural, conformational and functional information which is otherwise difficult to obtain. Various applications including those in inorganic chemistry have been reviewed from time to time[1-7]. The present report summarises some applications to organo-selenium compounds with emphasis on the work done by the Bangalore group

Experimental

NMR spectra of oriented molecules can be recorded on normal high resolution spectrometers. Suitable solutions[1-5] are prepared in liquid crystals and the spectra recorded with or without sample spinning depending upon whether the experiments are performed under the conditions that the liquid crystal director is along or orthogonal to the direction of spinning. A typical spectrum of dimethylselenium is shown in Fig 1. Line-widths of around 1-5 Hz are usually obtained in the spectra of oriented molecules.

For the selenium compounds, ^{77}Se has a natural abundance of 7.58% and spin ½ and ^{77}Se—^{1}H couplings can either be determined from studies of the selenium resonance or from the ^{77}Se—^{1}H satellites in the proton spectra. The latter technique is more common due to larger sensitivity of protons compared to selenium and also because the normally available spectrometers with facilities to study protons can be used. Furthermore, studies of the satellite spectra have the advantage that the information on the H-H and Se-H couplings can be obtained from the same experiment and the errors arising from the change of experimental conditions are avoided However, for the ^{77}Se-^{77}Se couplings and the ^{77}Se-chemical shift anisotropy studies, ^{77}Se-nmr may be necessary.

Fig. 1. NMR spectrum of oriented dimethylselenide. The spectrum is symmetrical about the dashed line and only half the spectrum to the right of the line shown. Liquid crystal solvent used : A mixture of N-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline and butyl-*p*(*p*-ethoxyphenoxycarbonyl)-phenylcarbonate Solute concentration : 9 mole per cent ; Temp. : 30° ; Spectrometer frequency : 100 MHz.

Basic principles

Though the basic principles of the technique are well known and documented, their brief presentation in this article is meaningful for the sake of completeness. Due to inherent molecular ordering and flow of the medium, the molecules dissolved in liquid crystal solvents show orientational effects and provide such information in the spectra which is otherwise not obtainable from the spectra in normal isotropic media. Such spectra for spin $\frac{1}{2}$ nuclei (i and j) contain information not only on the average values of the chemical shift $(\nu_i - \nu_j)$ and indirect spin-spin (J_{ij}) and direct dipole-dipole (D_{ij}) coupling tensors but anisotropic contributions of these second rank tensors can also be derived from the spectra. Of these, the most important parameters from the structural and the conformational points of view are the direct dipolar couplings and chemical shift anisotropy. Their determination and use will, therefore, be discussed in detail with emphasis to organoselenium compounds.

Having obtained the spectra, they are analysed using the standard procedures reported in the literature[1-8]. The analysis procedures are usually similar to those for the analysis of the spectra in the isotropic media except that the Hamiltonian contains additional terms due to various anisotropic contributions. The computer programs such as LAOCOONOR[8] or LEQUOR[9] are normally used.

The direct dipole-dipole coupling derived from the spectra of oriented molecules is related to the internuclear distance (r_{ij}) as in equation (1).

$$D_{ij} = \frac{\gamma_i \gamma_j}{4\pi^2} \cdot \frac{S_{ij}}{r_{ij}^3} \quad (1)$$

where γ is the magnetogyric ratio and S_{ij} is the degree of order of the axis ij.

The chemical shift anisotropy $(\Delta\sigma_i)$ for a nucleus in a 3-fold or higher symmetry axis is given by equation (2):

$$\Delta\sigma_i = \frac{3}{2} \cdot \frac{\sigma_{ia}}{S_{zz}} \quad (2)$$

where σ_{ia} is the chemical shift in the anisotropic medium with respect to that in the isotropic phase and S_{zz} is the order parameter of the symmetry axis.

Relations between other anisotropic and order parameters are reported in the literature[1-8].

The direct dipolar couplings derived from the analysis of the spectra of oriented molecules are used to determine molecular geometries with the help of equation (1). However, since the order parameters also have to be determined from the spectra, the number of independent dipolar couplings must at least equal the sum of the required order and geometrical parameters so as to obtain the necessary geometrical information without making assumption.

Equation (1) shows that if the order parameter and r_{ij}^3 are changed by a constant factor, D_{ij}'s and hence the spectra of oriented molecules remain unchanged. Since the order parameter has to be determined from the same experiment, the method provides relative internuclear distances rather than their absolute values.

A typical illustration of the determination of the structure of selenophene[10,11] (Structure 1) is given below before describing results on some other selenium compounds.

(2)H H(3)
(1)H H(4)
Se
(5)

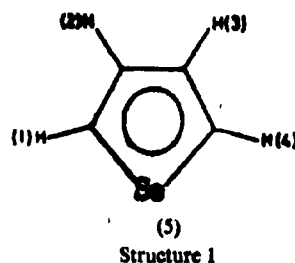
Structure 1

The analysis of the ^{1}H-nmr spectrum of selenophene with ^{77}Se-H satellites and without ^{13}C-H satellites provides four different interproton dipolar couplings, namely, D_{12}, D_{13}, D_{14} and D_{23} and two ^{77}Se-H couplings, namely, D_{15} and D_{25}. On the other hand only 3 independent ratios of the internuclear distances are necessary to describe the relative interproton and proton-selenium distances. Even after the determination of the molecular order, the system provides one additional coupling than that necessary for the determination of molecular geometry. Hence, in such a case the relative internuclear distances, i.e., r_{13}/r_{23}, r_{14}/r_{23} and r_{15}/r_{23} are determined by a least-square-fit computer programme which provides the geometrical and the order parameters such that the sum of the squares of the deviations between the observed and the calculated dipolar couplings is minimum. A computer programme referred to as SHAPE[12] is the one which is most commonly used for such a purpose. The values determined are shown in Table 1, including those derived from microwave spectroscopic studies. It may be mentioned that the proton nmr spectrum of oriented selenophene including ^{77}Se-H and ^{13}C-H satellites has in fact been studied and the carbon positions have also been determined. They are not included in the table for the sake of simplicity.

TABLE 1—RATIOS OF THE INTERNUCLEAR DISTANCES IN SELENOPHENE DETERMINED FROM NMR SPECTROSCOPY

Parameter	Value	
	NMR	Microwave
r_{13}/r_{23}	1.002±0.006	0.997
r_{14}/r_{23}	1.837±0.004	1.785
r_{15}/r_{23}	1.849±0.004	1.802

It may be mentioned that nmr spectroscopy of oriented molecules provides values in the liquid phase whereas other techniques such as X-ray, electron and neutron diffractions and microwave spectroscopy values are in the solid or the gaseous phases.

Applications

Selenium is an ideal nucleus from the point of view of nmr spectroscopy. The natural abundance of spin 1/2 isotope (^{77}Se) is reasonably large (7.58%) and the compounds provide relatively sharp lines. The proton nmr spectra of 1,3-dithiole-2-selone, 1,3-thiaselenole-2-thione and 1,3-diselenole-2-selone oriented in the nematic phases of N-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) or N-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA) show lines with widths less than 1.5 Hz on a WH-270 spectrometer and hence the observation of ^{77}Se-H and ^{13}C-H satellites in these systems present no special difficulties[13].

Several selenium compounds such as dimethyl-selenide[14,15], difluorophosphine selenide[16], selenophene[10,11], 2,1,3-benzoselenadiazole[17], benzo(b)selenophene[18], 1,2,5-selenadiazole[19], phenyl selenyl chloride and bromide[20], 3-phenyl-1,2,5-selenadiazole[21], tetraselenafulvalene[22], selenophene-2-carbaldehyde[23], 2,2′-biselenophene[24], trimethylphosphine selenide[25-27] and triphenyl selenophosphine[28] have been investigated in order to derive structural and conformational informations, and chemical shift anisotropies. In addition, 2-dimensional proton nmr spectrum of oriented 1-thia-3-selenole-2-thione has also been studied without ^{77}Se-H and ^{13}C-H satellites for the unique determination of ($J_{HH}+2D_{HH}$) – an information which cannot be obtained from the single resonance 1-dimensional spectrum[29,30].

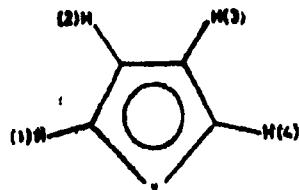
From the analysis of the proton nmr spectrum of dimethyl selenide with ^{77}Se-H satellites, the indirect spin-spin coupling between the protons of the two methyl groups has been determined as 0.1 Hz. A study of the spectrum including ^{77}Se-H as well as ^{13}C-H satellites has also been undertaken and the molecular structure derived. Assuming the inter-nuclear (C-Se) distance (r_{C}-Se) as 1.943 Å, a value of r_{C-H} as 1.073 Å has been obtained. The bond angles C-Se-C, H-C-Se and H-C-H have been derived as 95.7°, 106.22° and 110.14°, respectively. The C_3-symmetry axes of the methyl groups are displaced from the C-Se axes by 2.57° in such a way that the C-Se-C angle is reduced.

In difluorophosphine selenide, the SePF, FPF and SePH bond angles have been obtained as 116.8°, 98.1° and 118.6°, respectively.

The geometry-information in selenophene has been derived and the results are reported in the previous section. An interesting application has emerged from the studies on several heteroaromatic 5-membered ring systems (Structure 2). r_{14}/r_{23} has

(2)H H(3)

(1)H H(4)

X

X=O, N(H), C(H), S, P, Se, Te

Structure 2

been found to vary inversely with the van der Waals or covalent radii[31]. Values of these quantities have been determined for X=O, S, CH, NH, P, Se and Te.

The structure of 2,1,3-benzoselenadiazole has been derived from the proton nmr spectrum. Values of the indirect proton-proton couplings and the relative interproton distances indicate considerable bond fixation in the 6-membered ring of benzo-selenadiazole. In 1,2,5-selenadizole, for which the ^{1}H-nmr spectra including ^{13}C and ^{77}Se-satellites have been obtained, the interproton distance has been derived by assuming the ring geometry in addition to a scaling distance. The structure of the 6 and the 5 membered rings in benzo(b)-selenophene has been derived from its nmr spectrum in a lyotropic solvent.

Recently, very interesting new applications of nmr spectroscopy of oriented molecules have been discovered[32]. The studies involve recording the spectra in a mixture of 2 liquid crystals of opposite diamagnetic anisotropies. At a critical relative concentration of the two liquid crystals, it is possible to obtain spectra with two different types of molecular orientations if the temperature is suitably adjusted. The two orientations provide dipolar couplings in the exact ratio 1 : 2. The results are theoretically well understood[33]. These experiments provide spectral information which is otherwise not possible to derive from the spectra of oriented molecules. For example, separate determination of the indirect and the direct dipolar couplings between heteronuclei is possible only from such experiments. The method has been used to determine ^{77}Se-^{1}H indirect couplings in phenylselenyl chloride and bromide. The structural information in these systems has also been determined.

The preferred conformation of 3-phenyl-1,2,5-selenadiazole has been found to be twisted around the bond between the two rings and the angle of twist is $\simeq$ 20°. A comparison of the results with those in 3-phenyl-1,2,5-oxa and thiadiazoles in different solvents shows that the conformation is little influenced by the nature of the heteroatom at position 2 or the solvent. The molecule tetraselena-fulvalene is shown to be either puckered in a boat form or possessing a broad potential function for the puckering motion. The dihedral angle between the SeHC=CHSe and Se_2C=CSe_2 planes is 15.5 ± 0.6°.

In selenophen-2-carbaldehyde, the conformational information is derived by assuming that the positions of the 3 ring protons are the same as those in selenophene and considering either the existence of a single planar conformer or the *cis-trans* equilibrium. The existence of the Se-O *cis* conformer is confirmed though some evidence was also found for the presence of a small amount of Se-O *trans* conformer. 2,2′-Biselenophene has been shown to be present as an equilibrium between two twisted conformers, the transoid one being more abundant and the angle of twist being 25±5°.

The chemical shift and the indirect spin-spin coupling anisotropies have also been determined in some of the selenium compounds. The phosphorus-selenium indirect coupling constant in $PSe(CH_3)_3$ has been measured as −704 Hz. A comparison of the X-ray diffraction and nmr results in $PSe(CH_3)_3$ shows that the phosphorus-selenium indirect coupling is highly anisotropic. The ^{13}C and ^{31}P-chemical shift anisotropies in $(CH_3)_3PSe$ are 18 ± 10 and 99 ± 15 ppm, respectively. The C-P-C bond angle is 105.0 ± 0.2°. The ^{31}P-chemical shift anisotropy in triphenylphosphine selenide is determined as 103 ppm.

Conclusion

The survey provides an up-to-date information available from the spectra of oriented selenium compounds. The technique is potentially useful in the structural and conformational problems in selenium chemistry.

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ESR Study of Cu(II)-N-Aryl Glycinates

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Ten Cu(II) complexes of N-substituted phenylglycines, $RC_6H_4NHCH_2COOH$, have been synthesized (R = H, p-MeO, p-Me, p-Cl, p-NO_2, m-MeO, m-Me, m-Cl, m-NO_2 and o-Me). The powder esr spectra and magnetic susceptibility of these complexes have been measured and their structure and splitting of energy levels of Cu(II) ion in crystal field have been discussed in the light of the physicochemical data obtained

ESR study is a useful method to investigate crystal structure and to determine the ground state of electrons in the metal ion. For Cu(II) ion, its six coordinated compounds can not achieve the highest symmetry O_h because of the Jahn-Taller effect ; it can have only D_{4h} or lower symmetry if some other unsymmetrical factors exist If the unpaired electron of Cu(II) occupied the $d_{x^2-y^2}$ orbital as the ground state, there would be elongated distortion of the electron density of Cu(II) ion and the esr spectra would show $g_\parallel > g_\perp$. On the other hand, if d_{z^2} is the ground state, there would be compressed distortion and the esr would show $g_\parallel < g_\perp$. The majority of Cu(II) complexes show $g_\parallel > g_\perp$ which means that $d_{x^2-y^2}$ is commonly the ground state. In some cases, however, for complexes of $g_\parallel < g_\perp$ the ground state may still be $d_{x^2-y^2}$[1].

We have prepared ten Cu(II) complexes of N-substituted phenylglycines and have their powder esr spectra and magnetic susceptibility measured. Their structures and splitting of energy levels of the Cu II) ion have been discussed.

Experimental

Preparation of N-arylglycines :

All chemicals were of reagent grade. The synthesis of N-phenylglycine and N-(*para*-substituted phenyl)glycines have been reported previously[2] and the N-(*meta*-substituted phenyl)glycines are reported elsewhere[3]. The *ortho* substituted isomer, N-(o-methylphenyl)glycine, was prepared by the method of Walls[4].

Preparation of Cu(II)-N-arylglycinates :

The ligand was dissolved in dilute NaOH solution and pH adjusted to 7-8. To the ligand solution was added a half-equimolar solution of $Cu(NO_3)_2.3H_2O$. After 10 min of stirring the precipitate was filtered off and washed with water until free from nitrate ion. The solid product was dried below 70° for 8-12 hr. The results of chemical analysis of these Cu(II) complexes are given in Table 1.

Physical measurements :

Magnetic susceptibilities of the complexes were measured in a Gouy balance at room temperature using double distilled water, aqueous nickel chloride solution and $Ni(en)_3S_2O_3$ as the calibrants. The experimental and calculated magnetic moment values are also shown in Table 1.

The powder esr spectra of the complexes were measured at room temperature with a JES-3BX ESR spectrometer, equipped with 100 KHz field modulation unit. DPPH with g=2.0036 and Mn^{2+}-(MgO) were used as the standard field markers. The measured data of g_1(or $g_\parallel$), g_2(or $g_\perp$), g_3 and g_{av} of these copper(II) complexes are given in Table 2.

TABLE 1—ANALYTICAL DATA AND MAGNETIC MOMENTS OF Cu(II)-N-(SUBSTITUTED PHENYL) GLYCINATES

Substituent R	Molecular formula	Analysis %				Magnetic moment (B. M)		
		Nitrogen		Copper				
		Calcd.	Found	Calcd.	Found	Temp. K	Found	Calcd.
H	CuL_2	7.70	7.63	17.46	17.53	280	1.80	1.84
p-MeO	,,	6.61	6.80	14.99	15.03	281	1.85	,,
p-Me	,,	7.15	7.19	16.21	16.76	290	1.99	,,
p-Cl	,,	6.47	6.55	14.68	14.88	291	1.88	1.85
p-NO_2	$CuL_2.4H_2O$	10.65	10.79	12.08	12.09	290	1.95	1.94
m-MeO	$CuL_2.2H_2O$	6.09	6.24	13.82	14.16	285	1.88	1.85
m-Me	CuL_2	7.15	7.44	16.21	16.15	284	1.94	,,
m-Cl	$CuL_2.2H_2O$	5.98	6.26	13.56	13.58	289	1.91	,,
m-NO_2	$CuL_2.2H_2O$	11.44	11.43	12.97	13.16	281	1.85	1.84
o-Me	CuL_2	7.15	7.60	16.21	16.14	285	1.85	,,

TABLE 2—ESR DATA OF Cu(II)-N-(SUBSTITUTED PHENYL)GLYCINATES

Ligand	g_1 (or $g_\parallel$)	g_2 (or $g_\perp$)	g_3	g_{av}	ξ/Δ_1	ξ/Δ_2	ξ/Δ_3
PG	2.2248±0.0020	2.0646±0.0003		2.1193	0.02781	0.03115	
p-MeOPG	2.2256±0.0030	2.0664±0.0003		2.1208	0.02791	0.03205	
p-MePG	2.2273±0.0020	2.0667±0.0005		2.1216	0.02813	0.03220	
p-ClPG	2.2403	2.0854±0.0005		2.1383	0.02975	0.04155	
p-NO_2PG	2.4351±0.0040	2.0599±0.0030		2.2421	0.05410	0.02880	
m-MeOPG	2.2472±0.0030	2.0936±0.0004	2.0532±0.0004	2.1330	0.03061	0.04565	0.02545
m-MePG	2.2338±0.0010	2.0770±0.0010		2.1305	0.02894	0.03735	
m-ClPG	2.2488±0.0040	2.0787±0.0006		2.1369	0.03081	0.038[illegible]0	
m-NO_2PG	2.20[illegible]7±0.0006	2.1151±0.0006	2.0715±0.0009	2.1298	0.02480	0.05640	0.03460
o-MePG	2.1756±0.0030	2.0657±0.0030		2.1264	0.02166	0.03170	

Results and Discussion

For copper(II) ion in a crystal field, the magnetic moment (μ) was calculated by the first approximation method[5]

$$\mu^2 = 3/4\, g^2_{av} \quad \text{.. (1)}$$

$$g^2_{av} = 1/3(g_1^2 + g_2^2 + g_3^2) \quad \text{... (2)}$$

In a D_{4h} field, $g_1 = g_\parallel$, $g_2 = g_3 = g_\perp$. By substituting the g values obtained from esr spectra into the above equations, the corresponding μ values were calculated which are listed in the last column of Table 1.

It is seen from Table 2 that $g_\parallel > g_\perp$ for all the copper(II) complexes of N-arylglycines, which implies that the 3d unpaired electron of Cu(II) ion should occupy the $d_{x^2-y^2}$ orbital and it would have elongated distorted octahedral conformation. As $d_{x^2-y^2}$ is the ground state, the g's in a D_{4h} symmetry field should be

$$g_\parallel = g_e + \frac{8\xi}{\Delta_\parallel} \quad (3)$$

Fig 2

$$g_\perp = g_e + \frac{2\xi}{\Delta_\perp} \quad \text{... (4)}$$

while in a D_{2h} symmetry field,

$$g_1 = g_e + \frac{8\xi}{\Delta_1} \quad (5)$$

$$g_2 = g_e + \frac{2\xi}{\Delta_2} \quad (6)$$

$$g_3 = g_e + \frac{2\xi}{\Delta_3} \quad (7)$$

where g_e is the g value of free electron ($g_e = 2.0023$) and ξ is the spin-orbit coupling constant which is taken as 830 cm^{-1} for the free copper(II) ion. The significance of Δ value is shown in Fig. 1.

The various g values were obtained from esr spectra. When these g values were substituted into the above equations, the corresponding ξ/Δ values were obtained which are shown in the last three columns in Table 2

Fig 1 Ligand field splitting of d-orbitals in Cu(II) complexes

The shapes of the esr spectra of the complexes are shown in Fig 2.

In Fig. 2,(a) shows an axial pattern which suggests that the four atoms (N, N, O, O) are coplanar and are about equidistant from copper atom. Since the powder technique is not sensitive enough to resolve the two planar components(Cu—O, Cu—N), so that, should the true symmetry of these complexes be D_{2h} (*trans* configuration with six- or four-coordination) or even lower (*cis* configuration or *trans* configuration with five-coordination), the poor resolution obtained would still justify the use of D_{4h} symmetry.

These complexes may be considered to have the normal amino acid chelate type of structure (I of Fig. 3) in which the aromatic nitrogen atom and one of the carboxyl oxygen atoms act as donors while additional water molecules or the C=O oxygen atoms of neighbouring molecules further coordinated along the axis normal to the molecular

plane to form an elongated octahedral or square-based pyramidal configuration.

It is seen from Table 2 that for these complexes $\xi'/\Delta_\parallel < \xi/\Delta_\perp$ which means $\Delta_\parallel > \Delta_\perp$ indicating the ^2E_g level lies below the $^2B_{2g}$ level, and the order of the energy levels is

$$^2B_{1g}(d_{x^2-y^2}) < {}^2A_{1g}(d_{z^2}) < {}^2E_g(d_{xz}, d_{yz}) < {}^2B_{2g}(d_{xy})$$

When R=*m*-MeO, *m*-NO_2, [(b) and (c) in Fig. 2], the esr spectra exhibit three g values which fact indicates that the symmetry of these two complexes is lower than D_{4h} and their molecules would show a rhombic distortion due to the difference in Cu-O and Cu-N bond lengths. It is interesting to note that, although *m*-MeO group has lower electron attracting ability than *m*-Cl group[6], the esr spectra showed that the latter complex still has the same configuration as the unsubstituted Cu(II)-N-phenylglycine complex, which indicates that in addition to the effect of electron density change on the nitrogen atom of the ligand there must be some steric effect to elongate the Cu-N bond. It may also arise from different geometrical arrangement of the ligands in the complexes[7].

A comparison of the ξ/Δ values shows that the energy level sequences of these two complexes are as follows :

For Cu(II)-*m*-MeO_2PG complex :

$$d_{x^2-y^2} < d_{z^2} < d_{xz} < d_{xy} < d_{yz}$$

For Cu(II)-*m*-NO_2PG complex .

$$d_{x^2-y^2} < d_{z^2} < d_{xz} < d_{yz} < d_{xy}$$

The esr spectra of Cu(II)-*o*-MePG complex [(d) in Fig. 2] are quite different from the above mentioned types, suggesting low symmetry of the molecule and presence of exchange coupling[8]. According to Graddon[9], although there was no difficulty in making a four-coordinated model of chelate amino acid structure with *ortho* substituted N-arylglycinates, the substituents blocked access to the fifth and sixth coordination positions of the Cu(II) ion and also restricted the free rotation of the aryl group. Therefore, the *ortho* substituted ligand should from different configuration with Cu(II) ion than the other ligands. However, because of its weak chelating ability the *ortho* substituted ligand can hardly form a square planar configuration but very likely form a flattened tetrahedron with the four atoms (N, N, O, O) sitting out of a plane. This is a model of complex compounds having lower symmetry than the rest of the above mentioned complexes.

The esr spectra of the Cu(II)-*p*-NO_2PG complex [(e) in Fig. 2] is analogous to that of Cu(II)-*o*-MePG but with broader shoulder. Its line intensity was too weak to compare with the others and it became necessary to use larger quantity of sample to run the spectra. This means that the density of unpaired electron is very small. It may be ascribed to the strong electron attracting power of the *p*-nitro group that greatly reduces the electron density on the aromatic nitrogen atom of the amino acid and thus decreases its coordinating ability with Cu(II) ion. The complex can hardly be consistent with chelation of the amino acid type but most probably having a structure of the alkanoate type (II in Fig. 3) with

(I) (II)
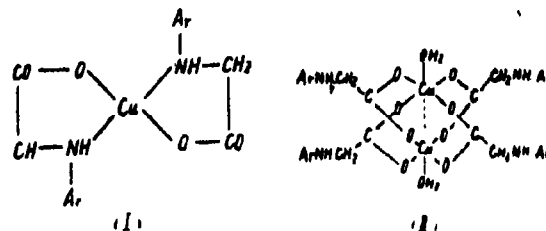
Fig. 3.

the aromatic nitrogen atom being non-donor. In this structure the distance between two copper atoms is short and exchange interaction exists so that a δ-bond can form by lateral overlap of the $3d_{x^2-y^2}$ orbitals of the adjacent copper atoms in the dimerized molecule.

An essential feature for interpreting the esr spectra of Cu(II)-amino acid complexes is the magnitude of parameter $\Delta g_\parallel$ ($\Delta g_\parallel = g_\parallel - g_e$). From equations (2), (3) and (4) it is seen that the reduction in $\Delta g_\parallel$ values may be due to an increase in Δ or a decrease in ξ or a combination of both. An increase in Δ and (or) a decrease in ξ will lead to decrease in $\Delta g_\parallel$, $\Delta g_\perp$ and Δg_{av}, which means an increase in covalency of the coordination bonding so as to increase the extent of delocalization of electrons from metal to ligand. On the other hand, a decrease in Δ and (or) an increase in ξ will lead to increase in $\Delta g_\parallel$, $\Delta g_\perp$ and Δg_{av}, which means increase in ionic character of the coordination bonding. Therefore, a plot of $\Delta g_\parallel$ against Δg_{av} may reflect the extent of covalency in the Cu(II) complexes formed with different N-aryl-glycines. Fig 4
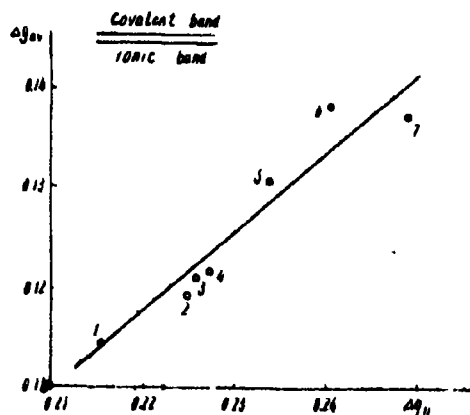
Fig 4

1 Glycine, 2 PG, 3 *p*-MeOPG, 4. *p*-MePG, 5. *m*-MePG, 6 *p*-ClPG, 7. *m*-ClPG.

shows such a plot, which indicates that an introduction of electron attracting group into the phenyl radical leads to increase ionic character of the metal-ligand bond. A comparison of $Cu(glycine)_2$[10] with

Cu(N-aryl-glycine)$_2$ shows that the former complex has higher covalency than the latter.

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Infrared Spectra of Iron(II) Complexes with N,N-Dimethylformamide and N,N-Dimethylthioformamide*

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Infrared spectra and assignment for the vibration frequencies are given for $Fe(DMF)_2Cl_2$, $Fe(DMF)_2Br_2$, $Fe(DMF)_6(ClO_4)_2$, $Fe(DMTF)_2Cl_2$, $Fe(DMTF)_2Br_2$, $Fe(DMTF)_2I_2$, $Fe(DMTF)_6(ClO_4)_2$ and compared with the spectra of the free DMF and DMTF The results are found to be in agreement with the bond length variation rules

AMIDES are coordinated to Lewis acids through the "hard" oxygen atoms of the C=O group whereas thioamides coordinate through the "soft" sulfur atoms of the C–S group. In order to compare the changes in bond lengths involved in coordination by both types of ligands the ir spectra of the following adducts of N,N-dimethylformamide (DMF) and N N-dimethylthioformamide (DMTF) have been studied: $Fe(DMF)_2Cl_2$, $Fe(DMF)_2Br_2$, $Fe(DMF)_6(ClO_4)_2$, $Fe(DMTF)_2Cl_2$, $Fe(DMTF)_2Br_2$, $Fe(DMTF)_2I_2$ and $Fe(DMTF)_6(ClO_4)_2$ In the ClO_4^- complexes the metal ions are in octahedrally coordinated by DMF and DMTF molecules, respectively and the anions are in outer sphere positions On the other hand, in tetrahedral halide complexes the halide ligands are coordinated in the inner sphere of the central iron(II) ion[1,2].

Experimental

The preparation of the complexes has been described previously[1]. The infrared spectra were obtained on a Perkin-Elmer 180 IR spectrometer. KBr pellets were used to measure the infrared spectra in the range from 4000 to 300 cm^{-1}, whereas Nujol mulls were used to obtain the spectra from 525 to 32 cm^{-1}. The preparation of the pellets and the nujol mulls were performed with freshly prepared complexes in a dry box filled with dry nitrogen gas[1]. The infrared spectra were also recorded under dry nitrogen atmosphere to prevent slow decomposition of the substances in contact with air-oxygen and air-water[1,2].

Results and Discussion

IR spectra and assignments for DMF and DMTF as given by Durgaprasad[3] and other

TABLE 1—INFRARED ABSORPTION BANDS (cm^{-1}) OF DMF AND THE IRON(II)-DMF COMPLEXES WITH THE ASSIGNMENT OF THE SIGNIFICANT VIBRATIONS

DMF (Lit.[3])	DMF	$Fe(DMF)_6(ClO_4)_2$	$Fe(DMF)_2Cl_2$	$Fe(DMF)_2Br_2$	Vibration*
		645 s			ClO_4^-
660 s	655 s	685 s	680 s	685 s	δ(OCN)
870 m	865 m	855 m	851 s	865 s	ν_σ(C'N)
		860 m			ClO_4^-
	940 m				ClO_4^-
1067 m	1067 m		1053 m	1060 m	r(CH_3)
1099 vs	1090 s		1110 s	1113 s	r(CH_3)
		1145 v			ClO_4^-
	1150 **	1160 s			r(CH_3)–
		1170 s			r(CH_3)–
1268 s	1255 s	1250 m	1245 m	1250 m	ν_{as}(C N)
1395 vs	1 85 s	1370 s	1372 s	1380 s	$\delta_\sigma(CH_3)$, ν(CN)
1410 s	1405 m	1415 m	1415 m	1405 v	δ(CH)
1410 **				1180 s	$\delta_\sigma(CH_3)$
1450 m	1440 s	1455 v	1430 s	1435 m	$\delta_{as}(CH_3)$
1512 m	1500 m	1490 m	1492 m	1500 m	$\delta_{as}(CH_3)$, $\delta_{as}(CH_3)$, ν(CN)
1685 s	1675 s	1640 s	1640 s	1650 s	ν(CO), ν(CN)
		1650 s	1650 s		
		1655 s	1655 s		

vs, s, m, w means very strong, strong, medium, weak, respectively.
* ν, δ, r, as and σ mean stretching, bending, rocking, assymetric, and symmetric, respectively.
** not resolved.

* Dedicated to Professor A. K. Dey on the occasion of his 60th birthday.

TABLE 2—INFRARED ABSORPTION BANDS (cm^{-1}) OF DMTF AND THE IRON(II)-DMTF COMPLEXES WITH THE ASSIGNMENT OF THE SIGNIFICANT VIBRATIONS

DMTF(lit.[8])	DMTF	$Fe(DMTF)_6(ClO_4)_2$	$Fe(DMTF)_2Cl_2$	$Fe(DMTF)_2Br_2$	$Fe(DMTF)_2I_2$	Vibration*
		625 s				ClO_4^-
		635 s				ClO_4^-
		680 w	680 w		680 w	
828 s	820 m	820 m	825 m	825 m	815 w	$\nu_{\sigma}(C'N)$
		850 m				ClO_4^-
970 s	970 s	968 m	948 s	935 s	940 m	$\nu(CS)$
1058 s	1050 s	1057 m	1050 w	1059 m	1059 m	$r(CH_3)$
		1110 s	1113 m		1110 m	$r(CH_3)$
1140 s	1128 s	1175 m	1136 s	1135 s		$r(CH_3)$
	1205 s	1200 m	1197 w	1195 w		$\nu_{\alpha}(C'N)$
		1250 w	1246 w	1240 w	1240 s	
					1353	
			1374 s	1378 m	1370 m	
1405 m	1400 s	1405 s	1406 s	1408 m		$\delta(CH)$
1410 sh	1410 **		1415 s		1420 s	$\delta_{\sigma}(CH_3)$
1420 vs	1420 **	1440 m	1432 m	1432 m	1420 m	$\delta_{\sigma}(CH_3)$
1450 s	1460 s	1460 m	1462 m	1462 m		$\delta_{\alpha}(CH_3)$
1472 s	1472 **		1492 m			$\delta_{\alpha}(CH_3)$
1560 s	1545 s	1570 s	1568 s	1570 s	1553 m	$\nu(CN)$

*, ** see table 1

TABLE 3—INFRARED ABSORPTION BANDS IN THE REGION FROM 525 TO 32 cm^{-1}

Compound	Absorption frequency cm^{-1}										
DMF	403			353	318	255					
$Fe(DMF)_6(ClO_4)_2$	415	397	384			239	220			142	
$Fe(DMF)_2Cl_2$	414		380	353	315	290	216			142	
$Fe(DMF)_2Br_2$	413		386	360	320	280	220	190	163	143	104
DMTF	519	403			274	215					
$Fe(DMTF)_6(ClO_4)_2$	516	407	393		308		174	140	130	100	
$Fe(DMTF)_2Cl_2$	505	403	343	325	295	215	190		136	117	
$Fe(DMTF)_2Br_2$	512	405		328	270	214				90	
$Fe(DMTF)_2I_2$	515	405	390	330	266			146			

authors[4-8] were confirmed. The data for the iron(II) complexes are given in Tables 1 and 2. The first bond length variation rule predicts[9] a lengthening of the bonds directly adjacent to the donor-acceptor interaction. In the complexes under study, these are the O=C and S=C bond in DMF and DMTF, respectively. The absorption line for DMTF at 970 cm^{-1}, assigned as S-C stretching vibration, is strongly lowered in the tetrahydral halide complexes and to a lesser extent in the octahydral perchlorate complex. The lowering of the O-C stretching frequencies of DMF at 1675 cm^{-1} is well pronounced both in the halide and the perchlorate complexes.

The comparison of the results obtained for the perchlorate complexes reveals that changes in the C=S bond lengths are smaller than in the C=O bond lengths, although the Fe-S bond appears stronger than the Fe-O bond. As back donation seems involved in the Fe-S bond, the S-C bond should be lengthened to a lesser extent than the C-O bond. This also means that differences in the outer sphere interactions with the ClO_4^- groups should exist. The changes in charge redistribution due to complex formation seem more strongly spread over the whole system in the DMTF complexes.

The second bond length variation rule[9] predicts a shortening of the C-N bond and a lengthening of the N-C′ bonds. In DMTF, the N-C′ stretching vibration at 1545 cm^{-1} is seen to be increased and hence the C-N bond shortened. In DMF, the N-C′ stretching vibrations are highly coupled so that the shifts due to complex formation could not be detected. Both, the symmetric as well as the assymmetric N-C′ stretching frequencies are found to be lowered by complex formation with DMF and DMTF complexes, respectively.

In agreement with the second rule a shortening of the C-H bond length was found, as can be seen from the comparison of the C-H stretching frequencies at 1405 cm^{-1} in DMF and at 1400 cm^{-1} in DMTF and the corresponding absorption lines of the complexes.

The bond length variation concept leads to the suggestion of a terminating group effect: changes in charge distribution due to a donor-acceptor interaction should be smaller with increasing distance from the site of the interaction but again more developed at the end groups of the complex[9]. The frequencies of the rocking vibrations at the (CH_3) groups in DMF and DMTF show indeed stronger changes than the frequencies of the C-H deformation frequencies.

The frequencies of the far-infrared absorption lines in the region of 525 to 32 cm^{-1} are presented in Table 3.

The Fe-halide stretching frequencies lie at 325, 315 and 270 cm^{-1} for $Fe(DMTF)_2Cl_2$, $Fe(DMF)_2Cl_2$ and the two bromide compounds, respectively. It can be seen, that the coordination of the Fe-central ion to the soft S-atom in DMTF leads to a weaker Fe-Cl bond than the coordination to the hard O-atom in DMF. Comparison of the ratio of the Fe-Br and the Fe-Cl frequencies with the square root of the atomic masses of Cl and Br show that the Fe-Br bond is by a factor of about 1.5 stronger than the Fe-Cl bond. Any differences between $Fe(DMTF)_2Br_2$ and $Fe(DMF)_2Br_2$ could not be resolved at the said line at 270 cm^{-1}. The Fe-I stretching vibrations should be found at frequencies between 212 and 207 cm^{-1} Because of the very weak Fe-I bond in these complexes (decomposition of Fe-I complexes takes place readily[9]) the line at 146 cm^{-1} should be assigned to this vibration The Fe S stretching vibrations are found between 343 and 393 cm^{-1}, whereby the highest values are found for the perchlorate- and the iodo-complex. In DMTF, these vibrations vary to a greater extent than the corresponding Fe-O vibrations found between 384 and 386 cm^{-1} [10-12]. The absorption lines at 220, 216 and 220 cm^{-1} are assigned to the O-Fe-O deformation frequencies of $Fe(DMF)_6(ClO_4)_2$, $Fe(DMF)_2Cl_2$ and $Fe(DMF)_2Br_2$[12].

The lowering of the line at 519 cm^{-1} at the DMTF complexes has been assigned to the lowering of the C-S stretching vibration (see Table 2) and not by the S-C deformation vibration which is involved in this complex coupled vibration. This may be deduced because the line at 215 cm^{-1} which is considered as the S-C-N deformation vibration is not significantly shifted. The line at 403 cm^{-1} in both DMF and DMTF is assigned to the C′-N-C′ deformation ferquency.

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Synthesis and Characterisation of μ-Oxo*bis*[oxotetrachlororhenates (VI)]

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$(Ph_4As)_2Re_2O_3Cl_8$ and $(Tz)_2Re_2O_3Cl_8$ have been prepared by the reduction of perrhenate with acetyl chloride and characterised on the basis of chemical analysis, spectral, magnetic moment and conductivity studies

VERY few oxo-bridged complexes of Re(IV), Re(V) and Re(VI) are known. Rhenium(IV) forms $K_4[Re_2OCl_{10}]$ in the reduction of potassium perrhenate by iodide in hydrochloric acid solution[1]. For Re(VI) and Re(V), only μ-oxodioxo-complexes are known. $Re_2^VO_3Cl_4(py)_4$ and $Re_2^VO_3Cl_4^{2-}(bipy)_2$ are prepared by reacting $ReCl_5$ with the ligand in wet acetone[2] or by reacting $ReOCl_4^{2-}$ or $ReOCl_3(Ph_3P)_2$ with the ligand in benzene[3]. $Re_2^VO_3(R_2dtc)_4$ complexes are obtained by reacting $ReOCl_3(Ph_3P)_2$ or $Re_2O_3Cl_4(py)_4$ with the dithiocarbamate ligand[4]. $Re_2^VO_3Cl_4(en)_2$ is obtained by standing $ReO(OH)(en)_2^+$ in hydrochloric acid[5]. The $Re_2^{VI}O_3Cl_8^{2-}$ anion is precipitated by partial hydrolysis on exposing chloroform solution of $ReOCl_4$ and Ph_4As^+ or Et_4N^+ chloride to atmosphere[6]. $Re_2^{VI}O_3Cl_6(ReO_3Cl)_2$ is obtained[7] by uv irradiation of a mixture of $ReOCl_4$, $ReOCl_4$-(H_2O) and ReO_3Cl.

We report here the synthesis of $(Ph_4As)_2$-$Re_2O_3Cl_8$ and $(Tz)_2Re_2O_3Cl_8$ compounds in good yield from potassium perrhenate.

Experimental

Materials: $KReO_4$ (J M) was dried at 120°. Ph_4AsCl (Fluka) and 2,3,5-triphenyl tetrazolium chloride (Sisco) were dried over P_2O_5 *in vacuo*. All the solvents and other chemicals were thoroughly dried by suitable methods. All experiments were carried out in glove box under oxygen-free dry nitrogen. Petroleum ether (60-80°) was used. AcOH-HCl was prepared by saturating acetic acid with hydrogen chloride gas.

Preparation of the compounds:

Tetraphenylarsonium salt: $KReO_4$ (0.400 g) was taken in acetyl chloride (10 ml) and kept for 40 hr. Ph_4AsCl (0.620 g) in AcOH-HCl (10 ml) was added to the red Re(VI) solution after filtration. The dark red precipitate formed was immediately filtered, washed with AcOH-HCl and dried *in vacuo* over NaOH for 6 hr.

Tetrazolium salt: To the clear red Re(VI) solution obtained as above were added 2,3,5-triphenyl tetrazolium chloride (0.482 g) in AcOH-HCl (5 ml) and acetyl chloride (5 ml). Shiny brown precipitate was obtained, filtered, washed with AcOH-HCl and dried as above

The yield is 85% in both the cases.

Elemental analyses and physical measurements: After alkaline peroxide fusion of the sample, rhenium was determined as tetraphenylarsonium perrhenate[8] and chloride as silver chloride[9]. The uv-vis spectra of solution were taken on a Beckman DU-2 spectrophotometer using 1 cm silica cell. Infrared spectra were rcorded with Beckman IR-20. Magnetic susceptibilities were determined by the Gouy method, packing the tubes under dry nitrogen in glove box. Molar conductances were measured with a Philips bridge PR9500/90 using a dip type microcell having a cell constant of 0.14 cm^{-1}.

Results and Discussion

The red and brown compounds are soluble in dichloromethane, acetone, nitromethane, acetonitrile but insoluble in benzene and carbon tetrachloride. The present method enables preparation of Ph_4As^+ and tetrazolium salts of $Re_2O_3Cl_8^{2-}$ ion in a very pure form. Their molar conductances, 150-180 $ohm^{-1}cm^2mole^{-1}$ in nitromethane, support their formulations as 2 : 1 electrolytes[10]. Their chemical analyses and other physical data are presented in Table 1.

The electronic spectra of the compounds in dichloromethane show the same peaks of Re(VI) as $Re^{VI}OCl_5^-$ and also confirm the hexavalent state of rhenium. The ε's of the peaks are similar but less than those[6] of $Ph_4AsReOCl_5$.

The ir spectrum of the tetrazolium salt is reproduced in Fig. 1; that of the Ph_4As^+ salt shows the same features. The ν(Re=O) bands are listed in Table 1. Rest of the bands in the region 4000-400 cm^{-1} are due to the cation. The compounds show three main bands at ~970, ~950 and ~910 cm^{-1}. In case of the arsonium salt, the two higher energy bands are split probably due to site symmetry. The above data suggest two possible structures I and II for the $[Re_2^{VI}O_3Cl_8]^{2-}$ ion with *cis* and *trans* terminal oxygens respectively to the oxo-bridge between the two rhenium atoms. A

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF μ-OXO*BIS* [OXOTETRACHLORORHENATES(VI)]

Compound and colour	% Re	% Cl	λ_{max}[b] nm (ϵ)				ν(Re=O)[c] (cm^{-1})	ν(Re-O-Re)[c] (cm^{-1})	Λ_0^d	μ_{eff}[e] (B.M.)
$(Ph_4As)_2Re_2O_3Cl_8$ Dark red	24.87 (25.30)[a]	18 47 (19.31)	300 (1971)	440 (908)	550 (160)	900 (18)	935 m, 945 m 968 w, 955 w	905 s	190	1.46
$(Tz)_2Re_2O_3Cl_8$ Brown	28.15 (28.59)	21.20 (21.82)	300	440	550 (117)	880 (6)	950 m, 975 m	915 s	176	1 48

a—values in parentheses are Calcd. values.
b—in dichloromethane.
c—in nujol.
d—molar conductance, ohm^{-1}cm^{2}mole^{-1}.
e—at R. T.

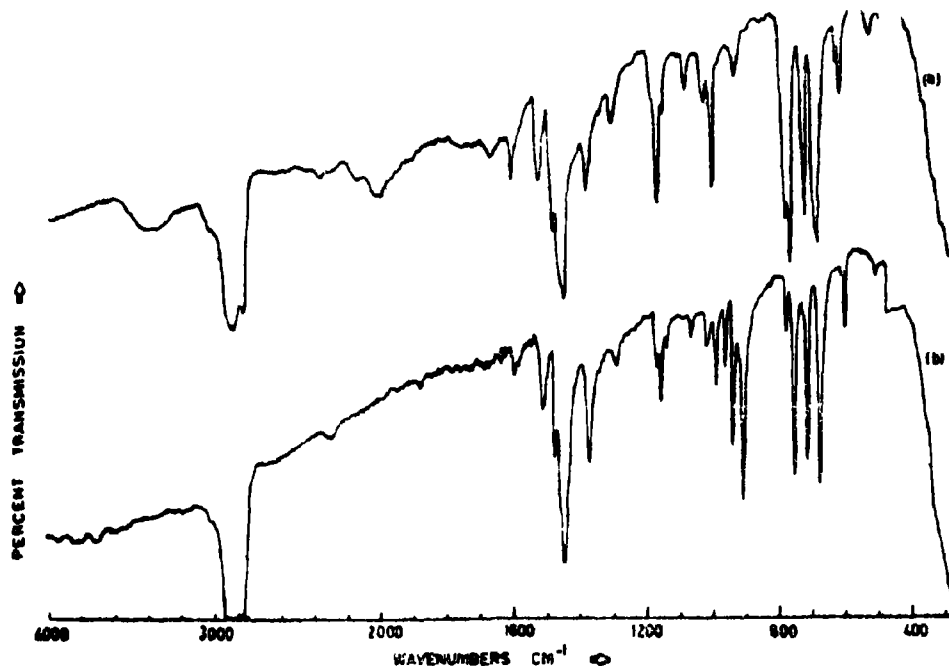
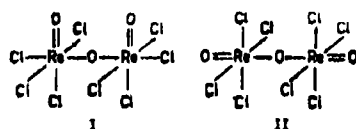



Fig 1. IR spectra (a) (TZ)Cl, (b) $(TZ)_2[Re_2O_3Cl_8]$ in nujol

linear bridge is assumed as it would permit better Re-O π-bonding than the bent one

I II

Structure

Structure II was assigned to the mauve products obtained by Brisdon and Edwards[6] on the basis of a doublet at 970 cm^{-1} suggesting a bond with terminal oxygen and a band at 730 cm^{-1} suggesting Re-O-Re, the lower value for the frequency indicating terminal oxygens in *trans* positions. This is supported by the weak paramagnetism of the compounds.

The antisymmetric Re-O-Re frequency for structure I is expected in the general range of frequencies, i.e., 800-950 cm^{-1}, found for oxygen-bridged halocomplexes[6]. Also, the reduced symmetry of the unit of the dimer might lead to splitting of degenerate frequencies and appearance of forbidden frequencies. So the bands at ~970 cm^{-1} and at ~950 cm^{-1} of the red to brown dimers can be assigned to the bond with terminal oxygen and the strong and somewhat broader band at ~910 cm^{-1} to Re-O-Re bonding having terminal oxygens in *cis* positions. It is, therefore, reasonable to suggest that these dimers have structure I. They show slightly reduced paramagnetism compared to $Re^{VI}OCl_5^-$ ion[6,11], due possibly to the exchange interactions. The antiferromagnetic coupling is weaker than that found for the *trans*-isomer by Brisdon and Edwards[6]. The presence of oxygens in *cis* positions to the bridge seems to weaken the antiferromagnetic coupling.

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Synthesis of *p*-Phenylene-di-Acrylyl-*Bis*-N-Phenyl (PAPHA), Fumaryl-*Bis*-N-Phenyl (FPHA), Isophthalyl-*Bis*-N-Phenyl (IPHA) Hydroxamic Acids and Spectral and Magnetic Studies of their Polymers with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)

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Three new *bis*-ligands, PAPHA, FPHA and IPHA have been synthesized and their polymers with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) have been prepared The compositions of the polymers have been proposed on the basis of elemental analysis, and their infrared and electronic spectra and magnetic susceptibilities have been reported On the basis of these observations, their structures have been discussed

EXCEPT for a cryptic mention of *bis*-hydroxamic acid-metal polymers[1], no other data appear to have been reported. A systematic study was therefore planned to undertake the synthesis of some *bis*-hydroxamic acids with the intention of studying their coordination polymers

Experimental

The chemicals used were of AnalaR or chemically pure grade.

Preparation of the ligands

In present investigations a modified method by Priyadarshini and Tandon[2] was used for the preparation of hydroxamic acids. In this procedure, freshly prepared N-hydroxylamine and vacuum distilled acid chloride in stoichiometric proportions are reacted at low temperature (0° or lower) in diethylether medium containing aqueous suspension of sodium bicarbonate.

Preparation of acid dichlorides Dry acid (0.1 m) (*p*-phenylene-di-acrylic-, fumaric- or isophthalic-) and phosphorus pentachloride (0.2 m) were taken in a dry 250 ml round bottomed flask fitted with an air condenser provided with a guard tube filled with anhydrous $CaCl_2$. The mixture was heated on a water bath till a yellow pulverised mass in case of *p*-phenylene-di-acrylic acid (12 hr) and a clear liquid in case of fumaric (4 hr) or isophthalic (2 hr) acid was obtained. Phosphorus oxychloride was distilled off under reduced pressure and the acid chlorides extracted in ether. *p*-Phenylene-di-acrylyl chloride was a yellow solid, fumaryl chloride a liquid and isophthalyl chloride a colourless crystalline solid.

Preparation of N-phenylhydroxylamine: N-Phenylhydroxylamine was prepared by controlled reduction of nitrobenzene[3]

Synthesis of PAPHA, FPHA and IPHA: Freshly prepared, crystallized, N-phenylhydroxylamine (0.25 m), diethylether (100 ml), sodium bicarbonate (0.3 m) and distilled water (30 ml) were taken in a 500 ml beaker and the mixture was cooled to 0° or below. To the above mixture, a solution of acid dichloride (0 1 m) in diethylether (150 ml) was added dropwise with constant stirring over about 1 hr. The product separated was filtered and washed thoroughly with saturated solution of $NaHCO_3$ to remove any acidic impurities.

These hydroxamic acids were crystallized from DMF-ethanol mixture. PAPHA and FPHA were yellow in colour (m.p.s. 225° and 194°, respectively), whereas IPHA was white (m.p. 180°). These hydroxamic acids have been reported for the first time in the present work and hence have been characterized on the basis of their elemental analysis and ir spectra The results are given in Table 1 and Tables 5 to 7, respectively.

TABLE 1—ANALYTICAL DATA OF THE LIGANDS

Sl. No	Ligand	Analysis % C Found (Calcd)	H Found (Calcd)	N Found (Calcd)
1.	PAPHA	71.4 (72.0)	5.11 (5.00)	6.84 (7.00)
2	FPHA	64.7 (64.4)	5.07 (4.69)	8 89 (9.39)
3.	IPHA	68.9 (68.9)	4.64 (4.59)	7.58 (8.04)

Synthesis of coordination polymers:

Polymers of PAPHA and FPHA with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II): Metal solution prepared by dissolving metal acetate (0.01 m) in DMF (25 ml) was added to a solution of *bis*-hydroxamic acid prepared by dissolving the ligand (0.01 m) on DMF (25 ml). The reaction mixture was heated on a water bath with constant stirring till the polymer separated as an insoluble solid. It was

then digested on a water bath for about 2 hr. cooled to room temperature, filtered, washed thorougly with DMF and ethanol and dried.

Polymers of IPHA with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II): Zn(II) polymer was prepared by a method similar to the one described above. Other metals however failed to yield insoluble products with this ligand in DMF. These polymers were prepared by the following procedure.

Metal solution, prepared by dissolving metal acetate (0.01 m) [metal acetylacetonate in case of Fe(II)] in DMF (25 ml) was added to a solution of *bis*-hydroxamic acid prepared by dissolving the ligand (0.01 m) in dioxane (25 ml) The remaining procedure was the same as above.

Polymers of PAPHA and FPHA with Fe(II): Ligand (0.01 m), metal acetylacetonate (0.01 m), ethanol (25 ml) and DMF (25 ml) were taken in a 250 ml beaker. The remaining procedure was the same as above.

Physical measurements: Magnetic susceptibility measurements were made on the solid polymers at room temperature with Gouys balance, using mercury tetrathiocyanatocobalt(II) as standard. Diamagnetic corrections were calculated by the method given in literature[4]. Visible and ultraviolet spectra were recorded in 300-1000 nm range with Karl Zeiss USU-2-p spectrophotometer. Infrared spectra of the ligands and the polymers were recorded on Specord-75 IR spectrophotometer in 400 to 4000 cm^{-1} region using nujol mull technique.

Results and Discussion

Tentative compositions for the polymers are proposed on the basis of elemental analysis. The proposed compositions, analytical data and colours of the polymers are reported in Tables 2 to 4. All polymers are insoluble in a wide variety of solvents and hence the products were purified by repeated washings with the solvents to remove all the unreacted metal ions and the ligand.

Infrared spectra: IR spectra of the polymers are practically identical. The frequency of some significant bands of the free ligand and of the metal-polymers are reported in Tables 5 to 7.

The free O-H stretching frequency appears at 3095 cm^{-1} in PAPHA, 3100 cm^{-1} in FPHA and at 3180 cm^{-1} in IPHA. Sharp band at 1595 cm^{-1} in PAPHA is assigned to C=O stretching vibration. Three consecutive bands at 1625, 1600 and 1570 cm^{-1} in FPHA and two bands at 1590 and 1610 cm^{-1} in IPHA are due to various resonating structures of R–N–OH (with –C=O attached to N). The N-O stretching vibration

TABLE 2—ANALYTICAL DATA AND COLOURS OF METAL-PAPHA(L) POLYMERS

Sl. No	Proposed composition of the polymer	Analysis % C Found (Calcd)	H Found (Calcd)	N Found (Calcd)	M Found (Calcd.)	Colour
1	$Mn_5L_4(OH)_2(H_2O)_2$	59 00 (59 48)	4.48 (4 03)	5 06 (5.78)	14.13 (14.18)	Dark brown
2	$(FeL\,2H_2O)_n$	62 50 (58 79)	5 27 (4 49)	4 96 (5.72)	10.80 (11.40)	Red
3	$(CoL)_n$	59 00 (63.03)	3 78 (3 94)	5.21 (6.13)	12.60 (12.89)	Dark brown
4	$Ni_2L(OH)_2(H_2O)_2$	50.05 (49.19)	4.65 (4 10)	4 52 (4.78)	20.05 (20.06)	Greenish brown
5	$(CuL)_n$	63.00 (62 40)	4 40 (3.90)	5.38 (6.07)	12.76 (13.77)	Green
6.	$(ZnL)_n$	61.10 (62 15)	4 18 (3 88)	5.75 (6.04)	13.23 (14.11)	Yellow

TABLE 3—ANALYTICAL DATA AND COLOURS OF METAL-FPHA (L) POLYMERS

Sl. No.	Proposed composition of the polymer	Analysis % C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	M Found (Calcd.)	Colour
1.	$Mn_5L_4(OH)_2(H_2O)_2$	50.20 (50.24)	4.63 (3.53)	6.76 (7.33)	16.56 (17.97)	Green
2.	$(FeL.2H_2O)_n$	50.35 (49.50)	4.26 (4.12)	6.76 (7.22)	13.87 (14.40)	Red
3.	$(CoL)_nH_2O$	50.25 (51.48)	4.46 (3.75)	7.12 (7.51)	15.97 (15.80)	Brownish yellow
4.	$(NiL\,2H_2O)_n2H_2O$	44.70 (44.99)	4.64 (4.67)	6.70 (6.56)	13.66 (13.76)	Yellow
5.	$(CuL)_n$	52.80 (53.40)	3.84 (3.34)	7.78 (7.79)	17.27 (17.67)	Green
6	$(ZnL)_n$	53.00 (53.13)	4.34 (3.32)	6.55 (7.75)	16.89 (18.09)	Yellow

TABLE 4—ANALYTICAL DATA AND COLOURS OF METAL-IPHA(L) POLYMERS

Sl. No	Proposed composition of the polymer	Analysis % C Found (Calcd)	H Found (Calcd)	N Found (Calcd.)	M Found (Calcd)	Colour
1.	$Mn_4L_3(OH)_2(H_2O)_2$	53 40 (54 23)	4 51 (3 61)	5 97 (6.33)	16.61 (16 55)	Greenish black
2	$(FeL\ 2H_2O)_n$	54 30 (54.81)	4 61 (4 11)	5.14 (6 39)	12 41 (12 75)	Red
3.	$(CoL\ 2H_2O)_n$	53.00 (54 43)	5.58 (4 08)	5 64 (6.35)	12 87 (13.36)	Light pink
4.	$(NiL\ 2H_2O)_n2H_2O$	49 90 (50.34)	4 16 (4 61)	5.35 (5.87)	12 06 (12 31)	Light green
5.	$(CuL)_n$	57.40 (58 60)	3 80 (3 42)	6.74 (6 84)	15.29 (15 51)	Green
6.	$Zn_2L_2(OH)_2(H_2O)_2$	49 65 (50.09)	4 14 (3 76)	5.16 (5 84)	20.84 (20.47)	White

TABLE 5—INFRARED SPECTRAL DATA (4000-400 cm^{-1}) OF PAPHA AND POLYMERS

PAPHA	Mn(II)-polymer	Fe(II)-polymer	Co(II)-polymer	Ni(II)-polymer	Cu(II)-polymer	Zn(II)-polymer	Assignment
–	3200-3600 b	3200-3600 b	–	3200-3500 b	–	–	H–O–H
3095 m	–	–	–	–	–	–	O–H
1595 s	1550 bsh	1510 sh 1585 s	1525 } m 1545 }	1540 m	1500 sh	1515 bsh	C=O
970 s	950 s	955 s	955 s	940 w	950 s	950 s	N–O
–	450 s 555 m 615 m	480 m 545 s	510 s	merged	570 s	520 m 555 w	M–O

b–broad, s–strong, bsh–broad shoulder; m–medium, sh–shoulder, w–weak

TABLE 6—INFRARED SPECTRAL DATA (4000-400 cm^{-1}) OF FPHA AND POLYMERS

FPHA	Mn(II)-polymer	Fe(II)-polymer	Co(II)-polymer	Ni(II)-polymer	Cu(II)-polymer	Zn(II)-polymer	Assignment
–	3200-3600 b	3200-3600 b	3200-3600 b	3200-3600 b	–	–	H–O–H
3100 m	–	–	–	–	–	–	O–H
1570 } 1600 } s 1625 }	1530 } 1550 } s 1555 }	1510 } 1565 } s 1575 }	1530 s 1545 } sh 1575 }	1525 } 1540 } s 1560 } 1570 }	1535 } s 1535 } 1565 sh	1525 s 1560 m	C=O
965 s	960 s	950 s	955 s	950 s	950 s	950 w	N–O
–	470 s 580 w	495 s 580 w	495 s 570 w	475 s	475 s	490 w 570 w	M–O

b–broad, s–strong, sh–shoulder, m–medium, w–weak.

TABLE 7—INFRARED SPECTRAL DATA OF IPHA AND POLYMERS

IPHA	Mn(II)-polymer	Fe(II)-polymer	Co(II)-polymer	Ni(II)-polymer	Cu(II)-polymer	Zn(II)-polymer	Assignment
–	3300-3600 b	3250-3600 b	3200-3500 b	3200-3500 b	–	3200-3500 b	H–O–H
3180 m	–	–	–	–	–	–	O–H
1610 } s 1590 }	1540 } s 1580 }	1500 } s 1520 } 1570 sh	1520 } 1540 } s 1555 } 1570 }	1530 m	1530 } m 1540 }	1525 m	C=O
950 s	970 s	970 w	960 w	960 w	960 s	970 w	N–O
–	460 w	540 m	–	–	510 s	500 bsh	M–O

b–broad; s–strong; bsh–broad shoulder; m–medium; sh–shoulder; w–weak.

is observed at 970, 965 and 950 cm^{-1} in PAPHA, FPHA and IPHA, respectively.

As anticipated, the O-H band disappears in the polymers. The carbonyl band is found to have been displaced towards lower frequency side indicating the formation of C–O. .M coordinate bond.

N–O stretching band is reported to be shifted towards higher frequency side with an increase in intensity[8]. The same is observed in case of IPHA polymers. However, it is found to have been shifted towards lower frequency side in case of PAPHA and FPHA polymers. There is no significant increase in the intensity.

The presence of a band in the region 3200-3600 cm^{-1} indicates the O-H stretching vibration of lattice or coordinated water wherever it is present

In all the cases the evidence of metal to oxygen (of the ligand) bonding is observed by a frequency at 450 to 615 cm^{-1} except in Co(II) and Ni(II)-IPHA polymers.

Electronic spectra and magnetic measurements

Electronic spectral data and magnetic data are summarised in Table 8

TABLE 8 –MAGNETIC AND ELECTRONIC SPECTRAL DATA OF POLYMERS

Sl No	Polymer	Effective magnetic moment B M	Absorption bands (kK)	Assignment
1	Mn-PAPHA	5 4187	28 57	$^6A_1 \to {}^4E(D)$
			23 80	$^6A_1 \to {}^4E(G)$
2.	Mn-FPHA	5 1584	27 77	$^6A_1 \to {}^4E(D)$
3	Mn-IPHA	5 2838	25 64	$^6A_1 \to {}^4E(G)$
4.	Fe-PAPHA	5 3197	18.51	C T
5	Fe-FPHA	5.3963	20 83	C T
6	Fe-IPHA	5 2510	17 85 } 14 49 }	C T
7	Co-PAPHA	5.1593	21 73 } 18 57 }	$^4A_2 \to {}^4T_1(P)$
8	Co-FPHA	4 5828	26 31	C T
9	Co-IPHA	4 9560	22.72 } 18.51 }	$^4T_{1g} \to {}^4T_{1g}(P)$
10.	Ni-PAPHA	3.1509	20 00	$^3T_1 \to {}^3T_2(P)$
			14.92	$^3T_1 \to {}^3T_1(P)$
			12 82	$^3T_1 \to {}^1E$
11	Ni-FPHA	2 8866	26.31	$^3A_{2g} \to {}^3T_{1g}(P)$ or C T
12.	Ni-IPHA	3 7521	22.72	$^3A_{2g} \to {}^3T_{1g}(P)$
			16.66	$^3A_{2g} \to {}^3T_{1g}(F)$
13.	Cu-PAPHA	1.9918	27.77	C. T
			14.28	$d_{yz}, d_{xz} \to d_{x^2-y^2}$
14.	Cu-FPHA	1.8823	27.77	C. T
			16.66	$d_{yz}, d_{xz} \to d_{x^2-y^2}$
			12.82	$d_{z^2} \to d_{x^2-y^2}$
15.	Cu-IPHA	1 8096	32.72	C T
			13 33	$d_{yz}, d_{xz} \to d_{x^2-y^2}$

Mn(II)-polymers : In Mn(II)-PAPHA polymer, two strong bands are observed at 28.57 and 23.80 kK which are assigned to $^6A_1 \to {}^4E(D)$ and $^6A_1 \to {}^4E(G)$ excitations, respectively. Only one band appears in FPHA-polymer at 27.77 kK which can be assigned to $^6A_1 \to {}^4E(D)$ excitation and one band at 25.64 kK in IPHA-polymer can be assigned to $^6A_1 \to {}^4E(G)$ excitation.

Moderate intensity of these bands is indicative of tetrahedral geometry.

The values of magnetic moment correspond to d^5, Mn(II) in all the polymers as reported in the literature[6]

Fe(II)-polymers : One band at 18.51 kK in PAPHA-polymer and at 20 83 kK in FPHA-polymer may be conveniently assigned to charge transfer[7]. Two bands at 17 85 kK and 14 49 kK in IPHA-polymer may also be assigned to charge transfer

The values obtained for the magnetic moment for all the polymers lie well within the range reported for octahedral high spin Fe(II) complexes.

Co(II)-polymers : Two bands at 21.73 kK and 18 57 kK in PAPHA-polymer are assigned to $^4A_2 \to {}^4T_1(P)$ excitation. Position of bands in the reflectance spectrum as well as magnetic moment of the Co(II)-PAPHA polymer suggest octahedral geometry. Elemental analysis, however, shows contradiction. Hence tetrahedral geometry is suggested for this polymer

One band at 26.31 kK in FPHA-polymer can be assigned to charge transfer. The spectrum of this polymer surprisingly does not show any band in the near infrared or visible region which can be assigned to d-d transition. Magnetic moment, and composition proposed on the basis of elemental analysis suggest tetrahedral geometry.

Two bands at 22.72 kK and 18 51 kK in IPHA-polymer can be assigned to $^4T_{1g} \to {}^4T_{1g}(P)$ transition suggesting octahedral geometry. Magnetic moment lies slightly lower than the calculated one which may be accounted for high orbital contribution

Ni(II)-polymers In FPHA-polymer a band appears at 26 31 kK which is assigned to $^3A_{2g} \to {}^3T_{1g}(P)$[8] transition or charge transfer. A band at 22.72 kK in IPHA-polymer can be assigned to $^3A_{2g} \to {}^3T_{1g}(P)$ transition and at 16.66 kK to $^3A_{2g} \to {}^3T_{1g}(F)$ transition. This is in good agreement with Liehr and Ballhausen[9] energy level diagram for Ni(II) ion in octahedral geometry.

The magnetic moment for Ni(II)-FPHA polymer lies well within the range generally reported for octahedral Ni(II) complexes[10]. The higher value obtained for IPHA-polymer may be due to the departure from octahedral geometry towards tetragonal (D_{4h}) geometry[11].

In Ni(II)-PAPHA polymer, a shoulder at 20.00 kK and two bands at 14 92 kK and 12.82 kK are assigned to $^3T_1 \to {}^3T_2(P)$, $^3T_1 \to {}^3T_1(P)$ and $^3T_1 \to {}^1E$ excitations, respectively indicating tetrahedral geometry. The value for magnetic moment lies lower than the value generally reported for tetrahedral Ni(II) complexes.

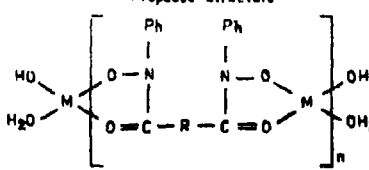
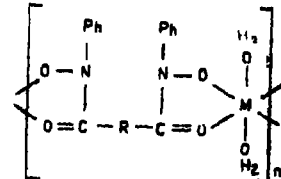
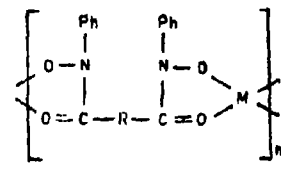
Cu(II)-polymers · In all the Cu(II)-polymers charge transfer bands are observed on higher frequency side of the spectra. Besides these, weaker bands are observed at 14.28 kK, 16.66 kK and 13.33 kK in PAPHA-, FPHA- and IPHA-polymers, respectively which are assigned to d_{yz}, $d_{xz} \to d_{x^2-y^2}$

transition. One more band at 12.82 kK in FPHA-polymer is assigned to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition.

From the reflectance spectra, all the Cu(II)-polymers can be assigned a distorted tetrahedral geometry. Magnetic data, however, show contradiction and suggest square planar geometry.

Zn(II)-polymers : These are diamagnetic and on the basis of elemental analysis, are suggested to be tetrahedral.

Proposed structures

The characterization of the polymers prepared in the present investigation is difficult because of their insolubility and intractibility. Their formation as polymers from steric considerations and assignment of degree of polymerization on the basis of elemental analysis are tentative.

The composition has been suggested on the basis of elemental analysis (Tables 2 to 4), which is explained later with the help of ir spectra, magnetic and reflectance studies and tentative structures have been proposed for these compounds.

The structures given for coordination polymers are always questionable. A simple linear, two dimensional planar or three dimensional structures are possible when the metal is coordinated to two, three or four ligand molecules, respectively. In the case of the polymer derived from methylene-*bis*-(5-salicylaldehyde) it has been suggested on the basis of some physico-chemical studies that two or three dimensional lattice structure predominates[18]. If the degree of polymerization is limited to certain extent then in such type of polymers the metal to ligand compositions may not correspond to that of linear chain polymer. Keeping these in view, linear chain unit structures proposed for the polymers may be taken as tentative ones.

Observations of the composition of some of the compounds lead to the conclusion that they should be simple polynuclear complexes, but their extreme

TABLE 9—PROPOSED STRUCTURES OF THE POLYMERS

Metal	n	R	Proposed structure
Mn(II)	n = 4	Where R = —HC=HC—C₆H₄—CH=CH—	$[(HO)(H_2O)M\{O—N(Ph)—C(=O)—R—C(=O)—N(Ph)—O\}M(OH)(OH_2)]_n$
Ni(II)	n = 1	Where R = —HC=HC—C₆H₄—CH=CH—	
Mn(II)	n = 3	Where R = —C(H)=C(H)—	
Mn(II)	n = 3	Where R = —C₆H₄—	
Zn(II)	n = 2	Where R = —C₆H₄—	
Fe(II)		Where R = —HC=HC—C₆H₄—CH=CH—	$[\{O—N(Ph)—C(=O)—R—C(=O)—N(Ph)—O\}M(H_2O)_2]_n$
Fe(II), Ni(II)		Where R = —C(H)=C(H)—	
Fe(II), Ni(II), Co(II)		Where R = —C₆H₄—	
Co(II), Cu(II), Zn(II)		Where R = —HC=HC—C₆H₄—CH=CH—	$[\{O—N(Ph)—C(=O)—R—C(=O)—N(Ph)—O\}M]_n$
Co(II), Cu(II), Zn(II)		Where R = —C(H)=C(H)—	
Cu(II)		Where R = —C₆H₄—	

insolubility makes one believe in their polymeric nature with more complex features present. The association of these low molecular weight units through hydrogen bonding or polymerization, making use of hydroxyl as bridging groups, cannot be ruled out. The structures proposed in Table 9 should therefore be taken as tentative in the light of the above discussion.

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Anthranilic Acid Hydrazide Complexes of Aluminium(III) and Titanium(IV)

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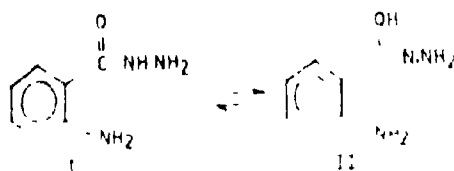
Anthranilic acid hydrazide (aaH) complexes of aluminium(III) and titanium(IV) have been synthesised by the reactions of isopropoxides and chlorides of aluminium(III) and titanium(IV) with anthranilic acid hydrazide in benzene. The complexes of the type [Al(OPr^i)$_{3-n}$(aa)], [AlCl$_{3-n}$(aa)$_n$] (where n = 1 or 2), [Ti(OPr^i)$_{4-n}$(aa)$_n$], [TiCl$_{4-n}$(aa)$_n$] (where n = 1-3) and (aa = anthranilic acid hydrazide anion) have been isolated All these complexes are partially soluble in chloroform, benzene and have been characterised on the basis of elemental analysis, ir and nmr spectral studies and electrical conductance measurements

THERE has been considerable interest in the chemistry of acid hydrazides and hydrazones because of their use in biological systems[1-4]. These hydrazides and hydrazones are versatile ligands due to several potential coordination sites[5].

Several transition metals complexes of various acid hydrazides and hydrazones have been reported[6,7]. However, no attempt has been made to synthesise aluminium(III) and titanium(IV) complexes of acid hydrazides Hence it was considered worthwhile to study the reactions of isopropoxides and chlorides of aluminium(III) and titanium(IV) with anthranilic acid which possesses labile protons attached to oxygen as well as nitrogen atoms. Such a study appears to be useful particularly because of the observations that 2-pyrolidinone possessing –NH and >C=O group, forms adducts with titanium(IV) chloride whereas in the reactions with titanium isopropoxide, a substituted product was obtained[8]. In view of the above, anthranilic acid hydrazide was chosen whose structure is depicted below

O ‖ C NHNH$_2$ NH$_2$ (I) ⇌ OH C=N.NH$_2$ NH$_2$ (II)

It is obvious from these structure that this ligand possesses one labile proton which is capable of undergoing amido-imido tautomerism.

Experimental

Glass apparatus with standard quickfit joints were used throughout the experimental work and stringent precautions were taken to exclude moisture. Benzene (AR, BDH), isopropanol (BDH) *tert*-butanol (SD'S) were dried and purified by standard method. $AlCl_3$ (BDH), $TiCl_4$ (Riedel), methyl anthranilate (Goldsun) and hydrazine hydrate (BDH) were used as supplied Isopropoxides of aluminium(III) and titanium(IV) were prepared by standard methods[9-11]. Anthranilic acid hydrazide was prepared by usual method and recrystallised from chloroform

The ir spectra were recorded on Perkin Elmer 621 spectrophotometer using nujol mulls, caesium iodide pellets or KBr pellets The nmr spectra were recorded on Perkin-Elmer R-32 spectrometer. Isopropanol was estimated by oxidimetric method[12] using 1 *N* $K_2Cr_2O_7$ in 12 5% sulphuric acid Chloride was estimated gravimetrically as silver chloride and nitrogen was estimated by Kjeldahl's method

Aluminium was estimated as aluminium oxinate Titanium was estimated as TiO_2 by direct ignition of compounds after digestion with ammonia and nitric acid in silica crucible. C and H were determined in the micro analytical laboratory of the Department of Chemistry, University of Delhi, Delhi

Reactions :

Reaction of isopropoxide of aluminium(III) with anthranilic acid hydrazide (*molar ratio 1 : 1*) : To a solution of Al(OPr^i)$_3$ (0 40 g ; 1.96 mmole) in benzene was added anthranilic acid hydrazide (0.30 g ; 1.96 mmole). A yellow suspension appeared at the time of addition The resulting mixture was refluxed for about 4 hr. The isopropanol liberated was collected azeotropically and estimated[12]. The excess of solvent was distilled off and the final product was dried under vacuum at 40°/0.5 mm when a white solid was obtained. Found : Isopropanol in azeotrope, 0.12 g ; Al, 8.6 , N, 13 9. Calcd. for [Al(OPr^i)$_2$(aa)] ; isopropanol in azeotrope, 0.12 g ; Al 9.1 ; N, 14.2%.

For the sake of brevity other reactions are given in Table 1.

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TABLE 1—REACTIONS OF ISOPROPOXIDES OF ALUMINIUM(III) AND TITANIUM(IV)

Sl. No.	Alkoxide g (mmole)	Acid hydrazide g (mmole)	Molar ratio	Time of refluxing hr	Product and their state	Amount of isopropanol in the azeotrope (g) Found (Calcd)	Analysis % Metal Found (Calcd.)	N Found (Calcd)	C Found (Calcd).	H Found (Calcd)
1.	$Al(Pr^i)_3$ 0.40 (1.95)	aaH 0.30 (1.95)	1:1	4	$[Al(OPr^i)_2aa]$ White solid	0.12 (0.12)	8.6 (9.1)	13.9 (14.2)	52.4 (52.9)	7.4 (7.8)
2.	$Al(OPr^i)_3$ 0.61 (2.98)	aaH 0.90 (5.96)	1:2	6	$[Al(OPr^i)(aa)_2]$ White solid	0.35 (0.36)	6.7 (6.9)	21.3 (21.7)	–	–
3	$Ti(OPr^i)_4$ 0.49 (1.72)	aaH 0.26 (1.72)	1:1	4	$[Ti(OPr^i)_3(aa)]$ Dark brown solid	0.10 (0.10)	12.6 (12.8)	11.0 (11.2)	51.0 (51.2)	7.9 (8.0)
4	$Ti(OPr^i)_4$ 0.58 (2.03)	aaH 0.62 (4.10)	1:2	6	$[Ti(OPr^i)_2(aa)_2]$ Dark brown solid	0.23 (0.24)	9.8 (10.3)	17.5 (18.0)	51.3 (51.5)	6.7 (6.8)
5.	$Ti(OPr^i)_4$ 0.31 (1.09)	aaH 0.50 (3.30)	1:3	12	$[Ti(OPr^i)(aa)_3]$ Dark brown solid	0.19 (0.20)	8.3 (8.6)	21.7 (22.6)	51.5 (51.7)	5.9 (6.1)

TABLE 2—ALCOHOLYSIS REACTIONS OF MIXED ISOPROPOXY ACID HYDRAZIDES DERIVATIVES OF ALUMINIUM(III) AND TITANIUM(IV) WITH TERTIARY BUTANOL (EXCESS)

Sl No	Mixed alkoxide derivatives (g)	Alcohol	Molar ratio	Time of refluxing (hr)	Product	Amount of isopropanol in the azeotrope (g) Found (Calcd.)	Metal % Found (Calcd)
1	$[Al(OPr^i)_2aa]$ (0.22)	Bu^tOH	1 : excess	5	$[Al(OBu^t)_2(aa)]$	0.09 (0.09)	7.9 (8.3)
2	$[Al(OPr^i)(aa)_2]$ (0.36)	Bu^tOH	1 : excess	3	$[Al(OBu^t)(aa)_2]$	0.05 (0.05)	6.6 (6.7)
3.	$[Ti(OPr^i)_3(aa)]$ (0.25)	Bu^tOH	1 : excess	6	$[Ti(OBu^t)_3(aa)]$	0.12 (0.12)	11.4 (11.5)
4.	$[Ti(OPr^i)_2(aa)_2]$ (0.28)	Bu^tOH	1 : excess	4	$[Ti(OBu^t)_2(aa)_2]$	0.07 (0.07)	9.4 (9.7)
5.	$[Ti(OPr^i)(aa)_3]$ (0.40)	Bu^tOH	1 : excess	4	$[Ti(OBu^t)(aa)_3]$	0.04 (0.04)	8.1 (8.4)

TABLE 3—REACTIONS OF CHLORIDES OF ALUMINIUM(III) AND TITANIUM(V) WITH ANTHRANILIC ACID HYDRAZIDE

Sl. No	Metal chloride g (mmole)	Acid hydrazide g (mmole)	Molar ratio	Time of refluxing (hr)	Product	Analysis % Metal Found (Calcd)	Cl Found (Calcd)	N Found (Calcd)	C Found (Calcd)	H Found (Calcd.)
1	$AlCl_3$ 0.48 (3.59)	aaH 0.54 (3.59)	1:1	20-22	$[Al(Cl_2)(aa)]$	10.6 (10.8)	28.1 (28.6)	16.8 (16.9)	33.3 (33.9)	3.4 (3.6)
2	$AlCl_3$ 0.28 (2.09)	aaH 0.63 (4.17)	1:2	24	$[AlCl(aa)_2]$	6.8 (7.4)	9.4 (9.7)	22.8 (23.1)	46.0 (46.3)	4.0 (4.9)
3	$TiCl_4$ 0.54 (2.84)	aaH 0.43 (2.84)	1:1	16	$[TiCl_3(aa)]$	15.1 (15.7)	34.6 (34.9)	13.2 (13.6)	27.2 (27.6)	3.0 (2.9)
4	$TiCl_4$ 0.29 (1.52)	aaH 0.46 (3.04)	1:2	20	$[TiCl_2(aa)_2]$	11.2 (11.4)	16.7 (16.9)	19.7 (20.0)	39.6 (40.0)	4.0 (4.2)
5	$TiCl_4$ 0.38 (2.00)	aaH 0.91 (6.01)	1:3	25-26	$[TiCl(aa)_3]$	8.7 (8.9)	6.5 (6.6)	23.3 (23.6)	–	–

Reaction between bis-*isopropoxy aluminium(III) anthranilic acid hydrazide complex with tertiary butanol*: To a solution of $Al(OPr^i)_2(aa)$ (0.22 g) in benzene was added tertiary butanol (excess) and the mixture was refluxed at bath temperature of 110-120°. The isopropanol liberated was fractionated azeotropically with benzene at 72-80°. The excess of solvent and tertiary butanol was removed under

reduced pressure, leaving a white solid mass. Found : Pr^iOH in azeotrope, 0.09 g ; Al, 7.9. Calcd. for $[Al(OBu^t)_2(aa)]$; Pr^iOH in azeotrope, 0.09 g ; Al, 8.3%.

The details of other reactions are given in Table 2.

Reaction between aluminium trichloride and anthranilic acid hydrazide (aaH) (molar ratio 1 : 1) : Anthranilic acid hydrazide (0.54 g ; 3.59 mmole) was added to a suspension of aluminium trichloride (0.48 g) in benzene (~50 ml). The mixture was refluxed in an oil bath for 20-22 hr when no more hydrogen chloride gas evolved. The reaction mixture was cooled at room temperature and excess of solvent removed under reduced pressure leaving behind a white compound Found : Al, 28.1 ; Cl, 9.6 ; N, 16.8. Calcd for $[AlCl_2(aa)]$; Al, 28.6, Cl, 10.8 ; N, 16.9%.

The other reactions are given in Table 3

Results and Discussion

A systematic study of reactions of isopropoxides and chlorides of aluminium(III) and titanium(IV) with anthranilic acid hydrazide in dry benzene has been carried out in different stoichiometric ratios The reactions proceed according to following equations :

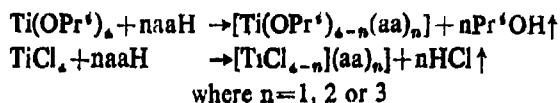
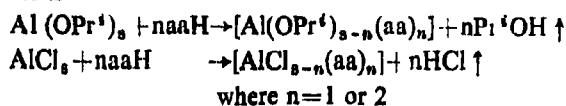
$$Al(OPr^i)_3 + naaH \rightarrow [Al(OPr^i)_{3-n}(aa)_n] + nPr^iOH \uparrow$$

$$AlCl_3 + naaH \rightarrow [AlCl_{3-n}(aa)_n] + nHCl \uparrow$$

where n=1 or 2

$$Ti(OPr^i)_4 + naaH \rightarrow [Ti(OPr^i)_{4-n}(aa)_n] + nPr^iOH \uparrow$$

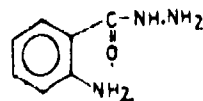
$$TiCl_4 + naaH \rightarrow [TiCl_{4-n}](aa)_n] + nHCl \uparrow$$

where n=1, 2 or 3

All these complexes are white to brown in colour and are soluble in dimethylsulphoxide and dimethylformamide. Electrical conductance, measured in dimethylformamide shows them to be non-electrolyte

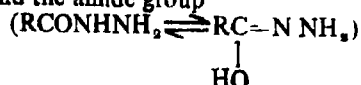
Molecular weight could not be determined because of their insolubility in most of organic solvents. Only two of the isopropoxide or chloride groups are replaceable by anthranilic acid hydrazide in case of aluminium, whereas in the case of titanium three isopropoxide or chloride groups are replaced This could be ascribed to steric hindrance or saturated coordination state of metals in these complexes, $[AlX(aa)_2]$ and $[TiX(aa)_3]$ (X=OPr^i or Cl) These complexes tend to decompose when heated under reduced pressure (0.01 mm)

IR spectra :

The important bands of the ligand are those which belong to amide, hydrazinic amino group vibrations. The amide group shows a number of bands due to combination of ν(C=O), ν(C-N) and ν(N-H) groups. In the spectra of ligand, the bands appearing in the regions ~ 1655-1645, 1560-1530, 1260-1250 may be assigned to amide I [ν(C=O)], amide II [(νCN+δNH)], amide III [(νCN+δNH)] vibrations, respectively[13,14]. The appearance of all these bands shows that the amide group in anthranilic acid hydrazide in solid state is present as such and not in its amido form. However, it may be pointed out that amide I absorbs at 1690-1650 cm^{-1} and the lowering of amide I is due to hydrogen bonding between ketonic and amino groups of ligands as depicted below.

C-NH.NH2
O
NH2

Accordingly, the amide group can coordinate to a metal atom through oxygen and secondary nitrogen atoms and it can also be involved in bond formation with metal atom through its imido oxygen or secondary nitrogen atom through deprotonation The bands around 3160 and 3300 cm^{-1} may be assigned to $\nu_{sym}NH_2$ and $\nu_{asym}NH_2$ vibrations Additional bands at 1620-1605 and 870-865 cm^{-1} may be assigned to $\delta(NH_2)$ and ρNH_2 vibrations

In the aluminium(III) and titanium(IV) anthranilic acid hydrazide complexes, the amide group vibration disappears on complexation and instead a strong band is observed at *ca* 1610 cm^{-1} It is likely that this band has its origin in ν(C=N) vibration which appears due to enolisation of the keto group, and the amide group

$$(RCONHNH_2 \rightleftharpoons \underset{\displaystyle HO}{\underset{|}{RC}}{=}N\,NH_2)$$

is involved in bonding with the metal atom through enolic oxygen of the amide group. The enolisation of amide group is also supported by the appearance of new bands in the region ~1580-1570 cm^{-1} attributable to ν(NCO) vibrations. It is worth mentioning here that the ν(C=N) vibration has significant contribution from $\delta(NH_2)$ vibration which occurs in the same region of the ligands. The involvement of enolic oxygen in anthranilic acid hydrazide complexes can be attributed to greater basicity of the ligand which facilitates the enolisation of amido group[15]. The coordination of amino group to metal atom in aaH complexes is indicated by a lowering of ν(NH) vibration (150 cm^{-1}) and diminishing intensity or disappearance of δNH band occurring at 750 cm^{-1}. The weak bands in the region 450-400 cm^{-1} may be due to νM-N vibration The changes observed in ν(NH) vibration in the complexes are not very conspicuous because of the presence of hydrazinic group which counterbalances any change occurring on coordination of amido group to metal. The strong band at ~535-550 cm^{-1} may be assigned to ν(M-O) while a peak at 1285cm^{-1} may be assigned to geminal dimethyl moiety of isopropoxy group[16]. The ν(M-Cl) absorbs at ~360-380 cm^{-1}.

NMR spectra :

The nmr spectra of the ligand show a complex multiplet at δ7.3 ppm due to phenyl ring protons, a doublet at δ(6.7-6.8) ppm assignable to protons of terminal hydrazinic amino group, doublet at δ(4.35-4.42) ppm assignable to -NH protons of -CO.NH group and finally a singlet at δ3.9 ppm, possibly due to protons of amino group.

On account of poor solubility, the nmr spectra of anthranilic acid hydrazide complexes were taken in deuterated dimethylsulphoxides. The spectra of anthranilic acid hydrazide complexes of titanium (IV) isopropoxide show a signal at δ4.0 ppm assignable to C-NH_2 group. This downfield shift indicates that the C-NH_2 group is deshielded. This is possible due to donation of lone pair of electrons by nitrogen to the titanium atom. The signal due to -NH protons of -CO.NH group δ(4 35-4.42) ppm disappears altogether, indicating that deprotonation takes place through secondary amide nitrogen as a result of bond formation with nitrogen atom in enolic form. The position of the signal of protons due to the terminal hydrazinic group remains unperturbed ruling out the possibility of coordination of amino group. The 1 : 1, 1 : 2 and 1 : 3 anthranilic acid hydrazide complexes of titanium(IV) show two signals at δ(1.20-1.52) ppm assignable to methyl protons of isopropoxy confirming the presence of isopropoxy group in these complexes

Thus, it appears that anthranilic acid hydrazide acts as mononegatively charged bidentate chelating agents having coordination sites at amino and enolic oxygen atoms, respectively

On the basis of the above studies, a polymeric structure can tentatively be assigned to these complexes. However, this may be confirmed by X-ray studies.

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Phenyl-Tin Cleavage by Some Ferrocenyl Hydrazones

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Ferrocenyl hydrazones of the type FcCH = N − NH − C(=O) − Ar [where Fc = C_5H_5Fe-C_5H_4 ; Ar = C_6H_5(I), C_6H_4Cl(II), $C_6H_4NO_2$(III), C_6H_4OH(IV) and C_5H_4N(V)] form stable tin derivatives when reacted with triphenyltin acetate in benzene solution Compound(I) gives hexacoordinated, octahedral tin(IV) complex, compound(II) gives penta-coordinated, trigonal bipyramidal tin(IV) complex, while compounds(III-V) give acetoxy bridged tin(IV) complexes which are dimeric in nature in solid form and monomeric in nature in chloroform solution. Evidences for their coordinated structures have been obtained from ir, pmr spectra and elemental analysis.

NELSON and Martin[1] have studied the interaction of chelating agents such as β-diketones, salicylaldehyde, 8-hydroxyquinoline with several organotin(IV) derivatives like tetraphenyltin, diphenyltin(IV) dichloride, triphenyltin chloride. They found that phenyl-tin cleavage is favoured at elevated temperatures, provided the ligand is present in high concentration. Such type of reactions can provide a convenient route for the preparation of new and interesting chelated tin compounds. Literature survey revealed no report on the interaction of chelating agents with triphenyltin acetate. In continuation of our studies on ferrocenyl hydrazones[2] we have investigated the reactions of some ferrocenyl hydrazones, FcCH=N-NH-C(=O)-Ar [Fc= $C_5H_5FeC_5H_4$, Ar=C_6H_5 (I), C_6H_4Cl (II), C_6H_4-NO_2 (III), C_6H_4OH (IV) and C_5H_4N (V)]

Materials and Methods :

Ferrocenyl hydrazones were prepared by the procedure reported elsewhere[2]. Triphenyltin acetate was purchased from Aldrich Chemicals and used without further purification All solvents were distilled and dried by standard procedures.

Preparation of tin(IV) complexes :

All the tin(IV) complexes were prepared by the following general procedure :

Triphenyltin acetate and ferrocenyl ligand in equimolar ratio were taken in benzene and the solution refluxed for about 8 hr. The hot mixture was filtered to remove insoluble impurities and the filtrate was concentrated under vacuum at 50°. The solid product thus obtained in almost quantitative yield was recrystallized from either benzene or chloroform and dried under vacuum. The compounds prepared along with their melting points and elemental analyses are given in Table 1.

Spectroscopic methods :

Infrared spectra were recorded on a Perkin-Elmer model 283B spectrophotometer using caesium iodide optics. PMR spectra were recorded on a Varian Associates Model T-60 spectrometer using tetramethylsilane as an internal standard.

Results and Discussion

Ferrocenyl hydrazones react with triphenyltin acetate in benzene at reflux temperature giving different kinds of tin derivatives. These tin deriva-

TABLE 1—ELEMENTAL ANALYSES OF PHENYLTIN(IV) COMPLEXES OF SOME FERROCENYL HYDRAZONES

Sl. No.	Compound	Composition	Yield %	m. p. °C	Analysis % C	H	N
1.	VI	$C_{48}H_{40}N_4O_2Fe_2Sn$	95	252	60.39 (61.67)*	4.69 (4.31)	6.12 (5.99)
2	VII	$C_{35}H_{29}N_2OClFeSn$	85	255	61.39 (60.50)	4.96 (4.60)	4.40 (4.00)
3.	VIII	$C_{32}H_{27}N_3O_5FeSn$	90	235	54.48 (54.30)	4.10 (3.85)	6.18 (5.94)
4.	IX	$C_{32}H_{28}N_2O_4FeSn$	78	214	58.19 (58.65)	4.76 (4.16)	3.91 (4.13)
5.	X	$C_{31}H_{24}N_3O_2FeSn$	80	232	57.56 (56.69)	4.47 (4.24)	6.11 (6.32)

* Figures with parentheses are Calculated values.

* NCL Communication No. 2929.

tives are stable and soluble in common organic solvents.

The elemental analyses of these compounds clearly show that reaction of ferrocenyl hydrazone compound I and triphenyltin acetate gives tin(IV) complex of the formula $(C_6H_5)_2Sn(L_2)$ (VI), (where L=ferrocenyl hydrazone anion). In this case both the phenyltin cleavage and elimination of acetoxy group have been observed. However, interaction of compound (II) with triphenyltin acetate is found to result in the elimination of acetoxy group only giving tin(IV) complex of the formula $(C_6H_5)_3Sn$-(L) (VII). Yet, interaction of compounds (III-V) is found to proceed in a different manner giving novel acetoxy bridged tin(IV) complexes of the formula $[(C_6H_5)_2SnL(OAc)]_2$ (VIII-X).

The infrared spectra of the ligands in Nujol[3] show strong N–H and C=O (amide I) stretching vibration bands around 3220 and 1650 cm^{-1}, respectively. The ν(N-N) band is found as a medium intense band around 920 cm^{-1}. The spectra of chelated tin(IV) complexes (Table 2) show the absence of absorption bands due to ν(N-H) and ν(C=O). Instead, two new bands are observed around 1605 and 1230 cm^{-1} which can be assigned to the stretching vibrational modes of conjugate >C=N–N=C< and C–O groups[3,4] A strong intense band around 1075 cm^{-1} can be assigned to phenyltin vibration[5]. This observation suggests that ligands enolize in solution and then bond with metal ions through replacement of amide proton In the spectra of all the metal complexes amide-II band is shifted to lower frequency by about 30 cm^{-1} while ν(N-N) band is shifted to a slightly higher frequency by *ca* 15 cm^{-1}. The negative shift in amide-II and the positive shift in ν(N-N) bands support the coordination through azomethine nitrogen atom. The characteristic bands of ferrocenyl moiety are observed as expected in the spectra. In the case of tin(IV) complex derived from compound IV, broad and weak bands centered around 2930 cm^{-1} attributable to the intramolecular -OH bonding are expected to be observed, but identification of these bands is not possible due to the presence of ligand vibrations in this region.

The spectra in the region 1600-1450 cm^{-1} are complex for all these compounds due to overlapping of several absorption bands. Although acetoxy group frequencies are difficult to locate due to the complex pattern of the spectra, the presence of acetoxy group in compounds VIII-X has been indicated by elemental analysis and supported by pmr spectral data.

The metal-ligand vibrational modes are generally found to occur in the far infrared region between 600-200 cm^{-1}. However, in the spectra of these complexes it is not easy to locate metal ligand vibrations because of the various skeletal vibrations of the ligands. In this study, the assignments made (Table 2) are purely tentative and based mainly on the information available in literature. The strong bands around 495 cm^{-1} can be assigned[6] to ν(Sn-O). The bands in the range 380-335 cm^{-1} and 610-600 cm^{-1} can be assigned to ν(Sn-N) and ν(Sn-C), respectively[7-9]

The pmr spectral data of tin(IV) complexes (Table 3) show the presence of acetoxy groups in the complexes VIII and X (methyl group protons at 2.10 ppm). The proton integration ratio shows the presence of only two phenyl rings in the complexes which again supports the phenyltin cleavage. The spectrum of compound VI shows phenyltin cleavage as well as the absence of acetoxy group in this compound. However, the spectrum of compound VII shows only the absence of acetoxy group and no loss of phenyl group.

In the case of all these compounds phenyl group protons appear around 7.16-7.33 ppm and azomethine proton at 7.06-7.16 ppm which is shifted down-

TABLE 2—IMPORTANT IR FREQUENCIES (cm^{-1}) OF PHENYLTIN(IV) COMPLEXES OF FERROCENYL HYDRAZONES IN NUJOL MULL

Sl No.	Compound	-C=N-N=C-	C-O	Sn-C	Sn-O	Sn-N	Sn-phenyl
1.	VI	1610 (s)	1240 (s)	610 (m)	560 (m)	370 (s)	1075 (s)
2.	VII	1610 (s)	1245 (s)	610 (m)	560 (m)	340 (s)	1070 (m)
3.	VIII	1600 (s)	1240 (s)	610 (w)	580 (s)	335 (m)	1075 (m)
4.	IX	1600 (w)	1240 (m)	610 (m)	555 (m)	360 (m)	1075 (m)
5.	X	1615 (s)	1260 (s)	615 (s)	560 (m)	380 (s)	1080 (m)

TABLE 3—PROTON CHEMICAL SHIFTS (δ) OF COMPLEXES DERIVED FROM TRIPHENYLTIN ACETATE

Sl. No.	Compound	Ferrocenyl group		Azomethine proton	Aromatic	Phenyl group	OCCH$_3$ protons
		Unsubstituted C_5H_5	Substituted C_5H_4				
1.	VI	3.9	4.33 4.86	*	8.23	7.4	–
2.	VII	3.9	4.4 4.9	7.16	8.23	7.4	–
3.	VIII	3.93	4.4 5.00	*	8.06	7.16	2.06
4.	X	3.91	4.23 4.83	7.06	8.00 8.66	7.33	2.12
5.	Triphenyltin acetate	–	–	–	–	7.43	2.00

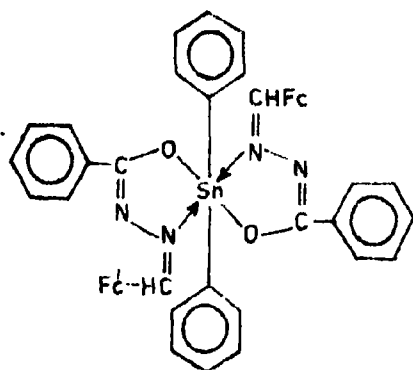
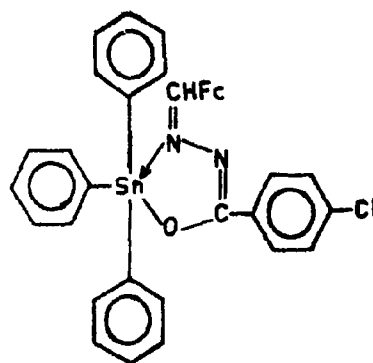
* Superimposed by peaks due to aromatic protons.

(Fc = Ferrocenyl group)

Fig 1

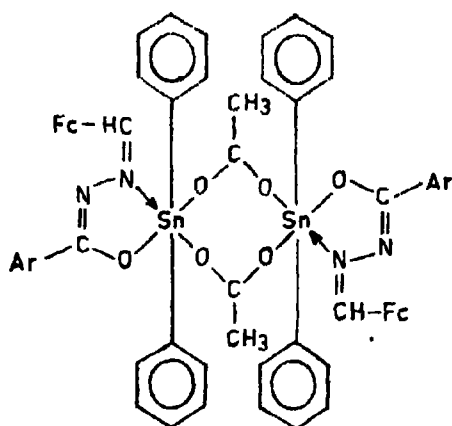
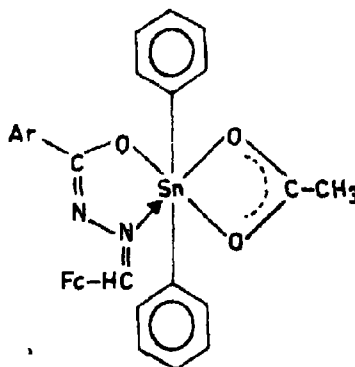
Fig 2

3a

3b

Fig 3

field by an order of 1.00 ppm This downfield shift is due to the chelation through azomethine nitrogen atom. Unsubstituted cyclopentadienyl protons appear as singlet at 3 8-4 3 ppm and protons of substituted cyclopentadienyl ring appear at 4 0-4 4 and 4.4-5 23 ppm as broad peaks as expected.

Structure of compounds VI *and* VII :

Elemental analysis and spectral studies indicate that compound VI may have the six coordinate, octahedral structure as shown in Fig. 1 and compound VII may have 5-coordinate trigonal bipyramidal structure (Fig. 2).

Structure of compounds VIII-X :

Although it is not possible to identify the characteristic acetoxy group absorption bands at 1540-1565 cm^{-1} in the infrared spectra of compounds VIII, IX and X in Nujol mull, a new band is seen at 1610-1620 cm^{-1} in the spectra of these compounds in chloroform solution The appearance of this new band is indicative of some structural changes in solution, but still suggesting a non-ester type of acetoxy group[10]. Accordingly, structures 3a and 3b (Fig. 3) can be tentatively suggested for these compounds, the solid compounds existing in dimeric form.

The molecular weight determination in chloroform (vapour-pressure osmometric method) shows the molecular weight to be in between the monomer and dimer, which again suggests that in chloroform solution these compounds may dissociate to monomer and an equilibrium between monomer-dimer exists

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Metal Complexes as Ligands : Binuclear Alkali Metal Complexes with Copper(II)- and Nickel(II)-Salicylaldimines

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The Schiff base complexes of nickel(II) and copper(II)-N,N'-disalicylidene ethylenediimine [M_aES] have been used as a bidentate ligand (complex ligand) in the synthesis of novel binuclear alkali metal complexes of the general formula [M_aES M_bL], M_aES acting as a bidentate complexing agent, coordinating through two phenolic oxygens to alkali metal salts M_bL (where, M_bL = Li, Na or K salts of 1-nitroso-2-naphthol, 8-hydroxyquinoline, anthranilic acid as well as alkali metal salts KSCN, LiCl, NaBr and NaI) The phenolic C–O link retained a considerable amount of partial double bond character in these binuclear complexes. The structure has been substantiated by infrared, electronic spectra and magnetic studies.

In recent years, the formation of oxygen bridged complexes containing two different ligands has become of interest to coordination chemists Transition metal complexes having phenolic oxygen atoms or β-diketone have been used as a ligand to study oxygen bridged complexes. Since all of these studies involved only transition metals, we thought it of interest to study the same phenomenon with the alkali metals.

As regards the study of alkali metals with due reference to the chances of complex formation, we have selected [*bis*-N,N'-ethylenebis(salicylideneiminato)copper(II)][1] and [*bis*-N,N'-ethylenebis(salicylideneiminato)nickel(II)][2] denoted as CuES and NiES, respectively as 'metal complex' ligands, and studied their behaviour.

The formation of oxygen bridged binuclear complexes from metal salicylaldimines (i.e , CuES or NiES) has been well established by Gruber *et al*[3-5] The CuES or NiES acts as a bidentate ligand in complexing with metal halides, $M'X_2$ (i e , $CuCl_2$, $NiCl_2$ etc.), to which it coordinates through the two phenolic oxygen atoms The crystal structure of the compound $(CuES)_2.NaClO_4$ has also been reported by Truter and coworkers[6] showing attachment of sodium with phenolic oxygen.

In view of the above, it was decided to extend the investigation by a systematic examination of the complexes of CuES and NiES with alkali metal salts (both organic and inorganic), which may be useful in understanding the transport and absorption mechanism of alkali metal ions from soil to plant.

Experimental

Our usual method of synthesis was to take CuES or NiES in a mixture of benzene and absolute ethanol (1 : 1), and to add alkali metal salts to it. The reaction mixture was then refluxed with constant stirring on a hot plate for about 12-16 hr. The whole thing went into solution and subsequently the adducts were precipitated in hot condition during the process of refluxing. They were filtered, washed with a mixture of benzene and absolute ethanol (1 : 1) and dried in an air oven at 90°.

Results and Discussion

The adducts are insoluble in benzene, ethanol and chloroform. They are stable under dry condition, but decompose on exposure to moisture ; as such, they were kept in a desiccator over anhydrous $CaCl_2$. The colour, decomposition temperature and analytical values of these complexes are given in Table 1 Detailed discussions of infrared spectra, magnetic properties and electronic spectra of binuclear alkali metal adducts have been done to establish their structure and bonding.

Infrared spectra :

Infrared spectra were recorded in Nujol mull for the ligands and the complexes between 4000-650 cm^{-1} Selected absorption bands in different regions are given in Table 1 and Table 2.

The most important feature is that while there are important differences between the infrared spectrum of CuES and NiES and the binuclear complexes formed when they act as ligand, the spectra of the various complexes are essentially the same, being independent of whether a transition or non-transition metal is bound to the complex ligand. The effect of coordination obviously will be the greatest for bands associated with the phenolic oxygen, and progressively less for linkages further from the coordination sites.

Table 2 gives the C=O infrared bands of CuES and NiES together with the binuclear transition metal complexes derived from them. Table 1 gives the C=O infrared bands of binuclear alkali metal complexes derived from CuES and NiES. Comparing the two tables for C=O infrared bands, we arrive at the conclusion that shifting of infrared bands for

TABLE 1

Compounds	Colour	Decomp. Temp. (°C)	% N		% Cu/Ni		% Alkali metal		C=O frequency near 1530 cm^{-1}	Magnetic moment at 27°
			Found	Calcd.	Found	Calcd.	Found	Calcd.		
CuES	Green	322							1532	1.90
CuES.Li1N2N	Light green	225	8.41	8.50	12 86	12.48	–	1.37	1538	2.1
CuES.Na1N2N	Yellowish green	228	8.61	8.00	12 40	12 10	4.30	4.38	1538	2 2
CuES.K1N2N	Yellowish green	240	8.00	7.77	11.68	11 74	7.35	7.21	1540	–
CuES.Na8HQ	Brown	250	8.19	8.45	12 39	12.78	4.65	4.65	–	1.91
CuES.K8HQ	Brown	255	7.86	8.19	12 62	12 39	7 63	7.60	1538	2.2
CuES LiAnth	Violet	240	8.46	8.88	13 37	13 43	–	1 48	1545	1.9
CuES.NaAnth	Violet	242	8.26	8.59	13.41	12 99	4 76	4 70	1542	2.1
CuES KSCN	Reddish violet	280	8 97	9 86	13 90	14 80	9.22	9.14	1555	1.9
CuES.LiCl	Pink	290	7.12	7.51	16.30	17 06	–	–	1538	1.9
CuES.NaBr	Reddish violet	290	5.88	6.47	14.46	14 68	5.35	5.31	1538	2.2
CuES.NaI	Pink	300	5.32	5.84	13.41	13 24	4 82	4.79	1555	1.9
NiES	Bright red	330							1536	Diamag.
NiES.Li1N2N	Yellow	255	8.38	8.33	11 89	11.65	–	–	1550	„
NiES.Na1N2N	Yellow	260	8 40	8.08	11 00	11 29	4.51	4.42	1550	„
NiES.K1N2N	Yellow	262	7.26	7.84	11 10	10.95	7.31	7.28	1550	„
NiEs.NaAnth	Reddish brown	252	8.65	8.68	12.81	12 13	4.80	4.75	1540	1.62
NiES.NaBr	Yellow	280	6.71	6.54	14 30	13.70	5.36	5.38	1543	1.92
NiES.NaI	Yellow	275	5.21	5.89	12.86	12 36	4 95	4 84	1550	Diamag

1N2N = 1-Nitroso-2-naphthol

8HQ = 8-Hydroxyquinoline

Anth = Anthranilic acid

TABLE 2—POSITION OF THE INFRARED BAND NEAR 1530 cm^{-1} (ASSIGNED TO C___O STRETCHING FREQUENCY) IN VARIOUS TRANSITION METAL COMPLEXES[7-11]

Compound	Frequency (cm^{-1})
X = CuES	1532
$X.CuCl_2$	1533
$X.ZnCl_2$	1551
$X_2\ Cu(ClO_4)_2.3H_2O$	1556
$X_2.Ni(ClO_4)_2\ 3H_2O$	1554
$X_2\ Mg(ClO_4)_2\ 3H_2O$	1555
$X_2Sr(ClO_4)_2.1\frac{1}{2}H_2O$	1549
$X_2\ Ba(ClO_4)_2$	1549
$X_2.AgClO_4\ 2H_2O$	1544
Y = NiES	1536
$Y\ CoCl_2$	1556
$Y_2\ Ni(ClO_4)_2\ 3H_2O$	1555
$Y_2.Co(ClO_4)_2.3H_2O$	1556
$Y_2.Fe(ClO_4)_2\ 2H_2O$	1553
$Z = (ZnES)_2$	1552, 1533
$Z\ ZnCl_2$	1554
$Z\ ZnCl_2.H_2O$	1538

both transition metal complexes and alkali metal complexes are virtually the same.

In the present complexes and bridged binuclear complexes derived from bidentate salicylaldimine complexes, 1530 cm^{-1} band was consistently shifted up by 15-30 cm^{-1} (Table 1 and Table 2), suggesting that this band may be due to the C=O stretching frequency in these compounds, rather than the C=N. This upward shift is due to the maintenance of a ring current arising out of electron delocalisation in the chelate ring.

Due to the delocalization of electrons towards the benzene ring, the ν(C=O) (phenolic) stretch is expected to occur at higher energy in comparison to the ν(C–O) (alcoholic) stretch[8a]. It is, therefore, suggestive that the phenolic C–O link attained a considerable amount of partial double bond character in these complexes. This is what is to be expected from the readiness with which these binuclear complexes were formed.

The above assignments were also found compatible with those made for the C=O links in metalacetylacetonates[8b]. This has also been supported by the observation that *bis*-(N-methylsalicylaldimino)zinc(II), which is known to be dimeric with two bridging and two non-bridging molecules per dimer[9], has a doublet band in this region (1534 and 1553 cm^{-1}).

Magnetic property :

Magnetic measurements were taken on Cahn-Faraday electronic balance at 27°. The results are recorded in Table 1.

The magnetic moment of CuES has been found to be 1.90 B.M., suggesting their square planar structure with coordination number 4. The binuclear alkali metal complexes have magnetic moment values in the range of 1 90–2 24 B.M., suggesting the same geometry of CuES in the alkali metal adducts.

NiES is diamagnetic, suggesting a square planar geometry with a coordination number 4 for Ni^{2+} ion. The binuclear complex compounds of alkali metal salts with NiES are also diamagnetic in nature (except NiES.NaBr and NiES.Na-Anth) suggesting the same stereochemistry of NiES in adducts. The slight deviation from strict diamagnetism in the case of NiES.NaBr and NiES.Na-Anth is generally indicative of one of the types of so called 'anomalous behaviour'.

Had Na.8HQ been attached to NiES through nitrogen of 8HQ and nickel ion, the Ni^{2+} ion would

have assumed 5-coordination stereochemistry. This would have resulted in the formation of a paramagnetic compound. On the other hand, if Na.8HQ had been attached by oxygen and nitrogen atoms of 8HQ (with Na^+ outside the coordination sphere) to the Ni^{2+} ion, the compound would have been a six coordinated octahedral nickel(II) complex, showing paramagnetism with a μ_{eff} value ~3.2 B M.

The μ_{eff} value for NiES.NaBr and NiES.Na-Anth are 1.92 B.M. and 1.62 B.M, respectively, which are very low compared to 3.4 B.M. We therefore conclude that coordination number of NiES has not been raised even in the case of NiES. NaBr or NiES.Na-Anth.

It is interesting to note that CuES formed complexes with all the three alkali metals (e.g. LiCl, NaBr, NaI and KSCN), while NiES formed only with sodium (i.e. NaBr and NaI). This may be due to the size of the metal ions and O–M–O distance of the ligand.

Electronic spectra :

All electronic spectra were recorded on Varian Cary-14 spectrophotometer in Nujol mull.

As a result of the distorted octahedral or square coordination of Cu(II), a detailed interpretation of its electronic absorption spectrum is somewhat complicated. We have not therefore studied the electronic spectra of alkali metal complexes derived from CuES Study of magnetic properties of the adducts derived from CuES is itself a sufficient evidence to establish the structure of these compounds.

The absorption band of medium intensity at 450 nm in electronic spectra of NiES suggests the square planar structure of Ni^{2+} with the coordination number 4, due to which it is bright red in colour. The absorption band of binuclear alkali metal complexes derived from NiES is found in the range of 450 nm to 500 nm, suggesting the same square planar geometry of NiES with coordination number 4 in all the alkali metal adducts. As the coordination number of Ni^{2+} in NiES remains the same in the adducts, it is clear that alkali metal salts are not attached through Ni^{2+} ion. No absorption band has been found in the range of 600 nm to 1200 nm in the binuclear alkali metal complexes. The absence of these bands in electronic spectra further confirms that the coordination number of Ni^{2+} in NiES binuclear alkali metal complex compounds have not been raised, but remains 4 with square planar geometry.

Structure and bonding :

In the present complexes, the complex ligands have two phenolic oxygens in the *cis* position and are forced to act as bidentate. The bonding between the salicylaldimine complex M_aES and the alkali metal is most likely to occur by dative bonding via the two phenolic oxygen atoms of the ligand which has been supported by the ir spectra, magnetic properties and electronic spectral studies of the adducts. The structure and bonding of the newly prepared compounds, of the general formula [M_aES. M_bL], may be what is shown in Fig. 1.
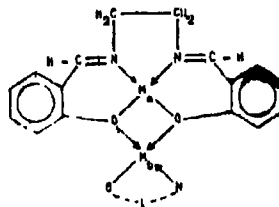
Fig 1. M_a = Cu(II) and Ni(II).
M_bL = Alkali metal salts of 1-nitroso-2-naphthol, 8-hydroxyquinoline, anthranilic acid and LiCl, NaBr, NaI and KSCN

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Application of Coordination Compounds of Silicon and Copper in Fiber and Fiber Reinforced Plastic Materials

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Some of the important characteristics of fiber reinforced plastic materials which make them significant as high specific strength, stiff, corrosion and fatigue resistant materials, have been described. Use of coordination compounds of copper and silicon has been particularly mentioned in view of their marked effect in increasing the strength of fibers in the case of carbon fibers and interfacial bonding between fiber and matrix for glass fiber reinforced plastics respectively. The coordination compounds of monovalent copper such as dichloro and diacetato and of silicon mainly aminosiloxanes help in cyclisation reaction resulting in considerable increase in the mechanical properties of carbon fibers formed which is ultimately reflected in the composite properties. The silicon coupling compounds having organic functional groups coordinated to silicon give, on treatment with a glass fiber, a relatively high surface energy which gives good wetting as well as bonding to the resinous matrix.

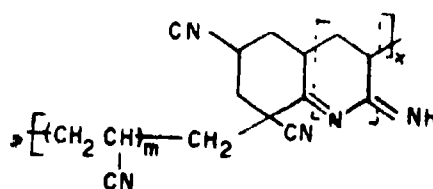
FIBER reinforced plastics[1-5] are finding increasing use as structural engineering materials because of their high strength and stiffness properties varying over a broad range. Carbon fibers and glass fibers have been extensively used in reinforced plastics for use in industrial applications such as aerospace, chemical, mechanical, marine, sports, agricultural and medical. The glass fiber reinforced composites are comparatively cheaper compared to carbon fiber reinforced plastics (CFRP) but have low specific stiffness. On the other hand CFRP have high specific stiffness which is maintained even at higher temperatures[2-6]. During the past two decades, tremendous efforts have been made to develop stiff reinforcing fibers and FRP materials[7-10]. New methods and techniques have been developed to make high strength high modulus carbon fibers. Newer compositions of thermosetting resins such as epoxy, phenolic and polyester and thermoplastic resins such as some polyester, polyethylene, polypropylene, nylon 6/6, etc have been made to suit specific requirements of FRP industry.

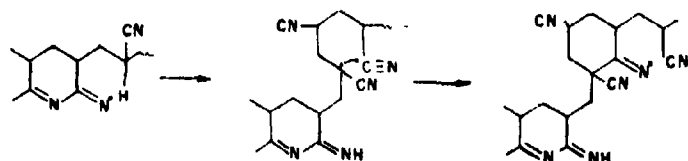
Carbon fiber is a newer form of carbon obtained by pyrolysing different organic fibers which are polymeric in character. Most extensively used precursors for carbon fiber preparation are polyacrylonitrile (PAN), jute, rayon, pitch etc[10]. The characteristics of carbon fibers produced depend on the nature of precursor and processing conditions. During the past decade considerable research and development activity have been going on in NPL for producing carbon fibers from different precursors.

Carbon fiber manufacture involves two main steps[11]:

1. Heat treatment in air or oxygen upto 300° to stabilize the precursor and convert the open chain structure of PAN to closed one.
2. Pyrolysis to 1000° in an inert atmosphere and heat treatment to 3000° in inert atmosphere, if desired.

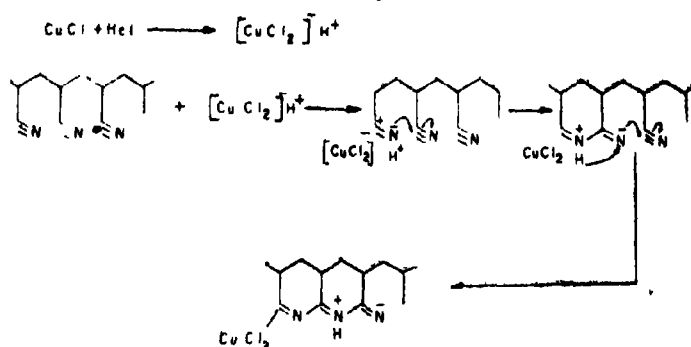
The most critical step in the manufacture of carbon fiber is the oxidation step which controls the overall properties of the carbon fiber formed. For many years constant efforts are being made to control this step in order to cut short the treatment time and to save energy along with improvement in the mechanical properties of the ultimate carbon fibers[12]. This can be brought about by incorporation of metallic additives in the form of coordination compounds such as dichloro or diacetato complexes of monovalent copper and aminosiloxane[13,14].

The oxidation step is done to produce thermally stable fibers so that they may not fuse when subjected to higher temperature. When pure PAN fiber is thermally treated in an inert atmosphere, the rearrangement of nitrile groups takes place at 200 to 300° giving a partially imperfect ladder type of cyclised structure represented by :

where m is generally in the range 0-2 and n in the range 0-5. This ladder type of structure is formed by free radical ionic mechanism. The free radicals are formed by the decomposition of defect structures in the precursor polymer. The amino radicals propagate and attack the next nitrile group or may abstract

a hydrogen atom terminating that particular sequence. Cyclisation takes place as indicated below :

This rearrangement or aligomerization of nitrile groups can be initiated at a lower temperature and the cyclization reaction can be accelerated by incorporation of reagents such as organic acids, inorganic acids and bases and metallic salts.

These reagents broadly (i) lower the temperature of initiation of cyclisation reaction, (ii) convert the sharp and intense exotherm observed in case of pure PAN into broader one and the ΔT is reduced to a much lower extent[14], (iii) the reagents provide a large number of initiation centers for cyclisation reaction thereby the cyclisation takes place in a much shorter time and the extent of cyclisation is increased to a much larger value

The cyclisation in presence of Lewis acids such as dichloro and diaceto monovalent copper ions takes place by ionic mechanism. The machanism is shown below :

$$CuCl + HCl \longrightarrow [CuCl_2]^- H^+$$

After the initiation, the reaction continues along the chain by stepwise ionic mechanism to produce ladder structure containing conjugated $-C=N-$ sequences. The fact that Cu is found in carbon fibers heated upto 1000° indicates that Cu is an integral part of carbon fiber.

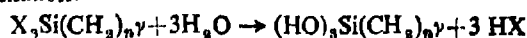
By use of dichloro Cu complex in the processing of carbon from PAN, the first step treatment time has been reduced to one third of the normal treatment time without the use of coordination compounds. Moreover, it has been found that the tensile strength increases by 30% while the Young's Modulus by 50%[15]. This clearly indicates the effective role of copper complex in improving mechanical properties of carbon fibers.

To make use of the excellent mechanical properties of the fibers, they have to be incorporated into a suitable matrix system. The interface between the filler such as carbon fiber or glass fiber and the resin has to be modified for effecting better adhesion and bonding The study of adhesion is related to several known effects such as :

1 Surface chemistry and physics of the components ,
2. The action of water and other potential weak bonding layers at the interface ;
3 The morphology of the matrix and the interface and
4 Mechanical requirements of the interface to allow distribution of shrinkages at areas of stress concentration

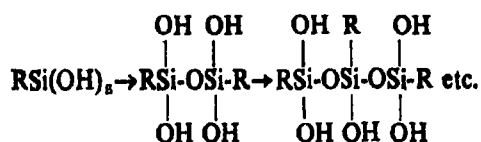
In case of carbon fibers, oxide groups such as carbonyl, carboxyl, hydroxyl, etc. are incorporated on the fiber surface by surface treatment[16,17] of the fibers, dry as well as wet It involves treatment with oxygen, ozone nitric acid, sodium hydroxide, sulphuric acid/potassium permanganate and different electrolytes such as hypochlorous acid, sodium hydroxide, etc.

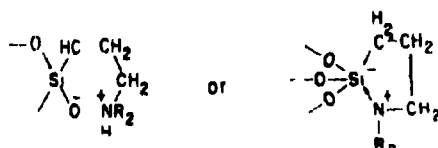
In glass reinforced plastics, marked improvement in properties is imparted by traces of appropriate reactive silanes at the interface. This indicates that the silane coupling agents[18-23] have an important role which improves the adhesion. The silane coupling agents are of the general structure $X_3Si(CH_2)_n y$ where n is 0-3, X is a hydrolysable group on silicon and y is an organo functional group selected for compatibility with the given resin matrix. Most of the silane coupling agents are applied to glass fiber surface from aqueous solutions. The hydrolysable groups are therefore essential for generating intermediate silanols.

$$X_3Si(CH_2)_n y + 3H_2O \rightarrow (HO)_3Si(CH_2)_n y + 3\ HX$$

The compositions of silane coupling agents in dilute solutions depend on the organo functional groups and the pH of the solution The silanes hydrolyse to give triols and then condense slowly to

oligomeric siloxanols.

$$RSi(OCH_3)_3 + 3H_2O \rightarrow RSi(OH)_3 + 3CH_3OH$$

$$RSi(OH)_3 \rightarrow RSi(OH)_2\text{-}O\text{-}Si(OH)_2\text{-}R \rightarrow RSi(OH)_2\text{-}O\text{-}Si(R)(OH)\text{-}O\text{-}Si(OH)_2\text{-}R \text{ etc.}$$

Amino organo functional silane coupling agents show unique solution properties when nitrogen is on the 3-carbon atom. Since it is well known that the cyclic five or six membered chelate ring have extra stability, the low molecular weight siloxanes with internal cyclic zwitter ion structures are formed in aqueous solution of three amino substituted organic silanols.

—O HC CH₂ Si CH₂ O NR₂ H or O O—Si O C CH₂ N—CH₂ R₂

Therefore, all commercial amino functional silane coupling agents have the nitrogen atom on the 3-carbon atom.

The silane coupling agents are not generally deposited on the fiber surface as simple oriented mono molecular films, but as multilayers with variable orientation depending upon condition of deposition[10]. A major portion of the deposited film is removed readily by water or organic solvents, but a small residue of the coupling agent is retained tenaciously by the surface which is effective in improving composite properties. Silanols, alkoxy silanes or chloro silanes applied to glass fiber under mild conditions are adsorbed physically through hydrogen bonding with surface silanol group. Under more strenuous conditions of temperature or catalyst the silanes bond chemically with the surface through siloxane linkages. These compounds are stable to air and water vapour. Another method of bonding chemically a coupling agent to the glass surface is to react with a difunctional Grignard reagent to give a firmly bonded organo functional group. Use of a flourinated glass surface is also known.

The chemical mobility of coupling agents attached to glass surface through hydrolysable bonds appears to be beneficial to composite properties. There is no correlation between polarity of silane or wettability of silane treated glass and the effectiveness of the silane coupling agent. For example, glass treated with chloropropyl silane coupling agent has a relatively high surface energy and is readily wetted by resins. Such treatment is ineffective with polyesters and phenolics but is quite effective with epoxides where chemical reaction is possible between the chloropropyl groups and the epoxy curing agent.

Wetting studies on silane treated glass are futile in arriving at the primary mechanism of adhesion through silane coupling agents since the interface between coupling agent and resin disappears preparation of composites. Better wettin allow complete displacement of air from tl surface and reduce the number of voids composite. The amount of silane couplin required on a glass surface to impart good m cal performance to a glass resin composite small to be measured by analytical means. T of radio active tracers has been made an been confirmed that the amount required proper silane to function as coupling agent less than the amount required of the silane t a monomolecular layer on the glass surface. coupling agents are equally effective when ad integral blends in resins. The silane, by cor with the polymer, modifies the morphology interface to improve stress transfer at the ir and resistance to water. This almost in involves a tightening up of the polymer st through increased crosslinks and rigidity. Th the silane should have maximum reactivity w polymer.

The silane coupling compounds can be pr by a number of methods involving chemical i tion of silicon containing compounds with i acid and organic functional groups. Trichlo tetrachloro silanes have been extensively u starting material for interaction with the compounds for introducing organo fur groups in the structure. The conditions reaction depend on the type of coupling required Trichloro and tetrachloro silane been prepared in NPL by interaction of ferro with mineral acid and then separating the methods of fractional distillation. The pro and purification techniques have been stand and the silanes have been prepared to the pu 99.9%. The silanes were treated with alcoh compounds of general formula Si(OR) $SiH(OR)_3$ were synthesised The compou thermally stable It is planned to prepare a of organo-silicon derivates from silane fo coupling agents.

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Mössbauer Spectra of Copper Nickel Ferrites

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Mössbauer spectra of the compositions $Cu_{1-x}Ni_xFe_2O_4$ ($0 \leq x \leq 1$) have been studied. For $x \leq 0.2$, the compounds are tetragonal and the rest are cubic spinels. Cation distribution obtained from the split lines of the Mössbauer spectra does not agree with that obtained from magnetisation data. The spectra seem to be complicated due to the presence of more than one hyperfine field at the B site Fe^{3+} owing to the distorting effect of the Cu^{2+} ion on the A sites. This leads to non-Lorentzian line shapes and excludes straight-forward calculation of cation distribution from relative areas under resonances.

MAGNETIC properties of spinel ferrites are strongly dependent on the nature of the cations and their distribution between the tetrahedral (A) and octahedral (B) sites in the cubic close packed oxygen lattice. $CuFe_2O_4$ is particularly interesting in this respect because the distribution of Cu^{2+} ions between the nonequivalent sites is temperature sensitive. Moreover, the presence of Cu^{2+} ions leads to severe Jahn-Teller distortion making the nonequivalent sites more distinct than in other spinels[1].

Nickel ferrite is an inverse spinel. It is interesting to see how the distribution of Cu^{2+} ions in the A and B sites are affected in the presence of Ni^{2+} ion which has a strong octahedral site preference. This prompted us to determine the cation distribution in the $Cu_{1-x}Ni_xFe_2O_4$ system ($0<x<1$) by magnetisation measurements (Kiran *et al*[6]). Several reports have appeared in the literature on the Mossbauer spectra of $CuFe_2O_4$ and $NiFe_2O_4$ (Evans and Hafner[1], Yamadaya *et al*[2], Evans *et al*[3], Sawatzky *et al*[4], Morel[5]), but no report has been made on the Mossbauer study of the mixed ferrite system $Cu_{1-x}Ni_xFe_2O_4$. This is being reported in this paper.

Experimental

The compounds were prepared by mixing appropriate quantities of CuO, NiO and α-Fe_2O_3 (all AR grade) and firing at 1320 K for 24 hr. The samples were then cooled slowly to 1020 K, annealed at this temperature for 48 hr and cooled to room temperature at 60°/hr. All the samples were characterised as monophasic solid solutions by X-ray diffraction (XRD).

Mossbauer spectra were recorded on a multichannel analyser (MCA 38A of ECIL) in the constant acceleration mode. The source used was ^{57}Co in rhodium matrix. The spectrometer was checked for velocity calibration by comparing the line positions of various standard absorbers (SS 310, pure iron foil and α-Fe_2O_3). The spectra were analysed using a computer program which performs a least mean square fit of the Lorentzian lines to the experimental points.
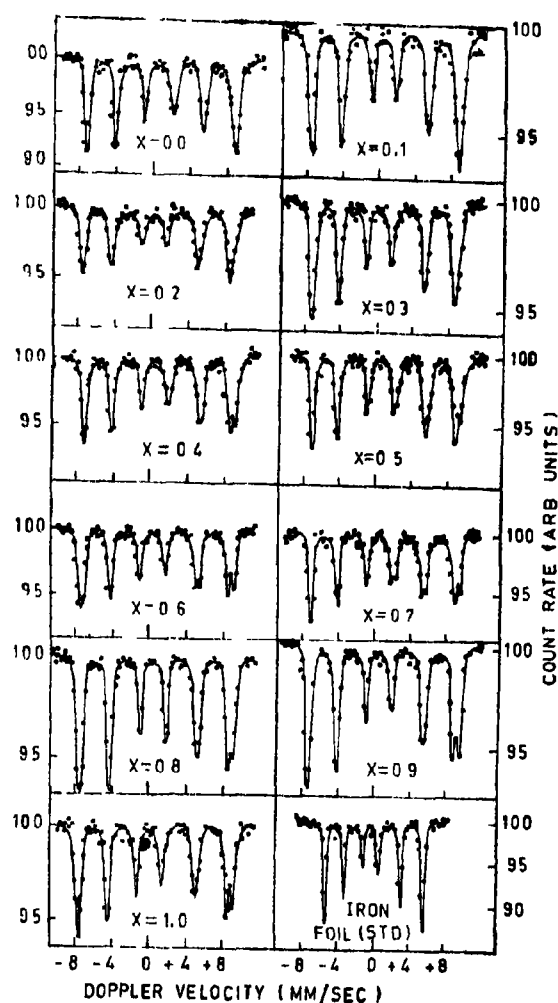
Fig. 1. Mössbauer spectra of the system $Cu_{1-x}Ni_xFe_2O_4$.

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TABLE 1—MÖSSBAUER SPECTRAL PARAMETERS+ OF $Cu_{1-x}Ni_xFe_2O_4$

Composition x	Lattice parameter a (Å)		Hyperfine field H_{eff} ± 5kOe A	Hyperfine field H_{eff} ± 5kOe B	Isomer shifts IS (mm/sec) A	Isomer shifts IS (mm/sec) B	Quadrupole splittings QS (mm/sec) A	Quadrupole splittings QS (mm/sec) B	Intensity ratio I_B/I_A	$\left[\frac{Fe_B^{3+}}{Fe_A^{3+}}\right]$†
0.0	a = 8.268, c = 8.607	T	492		0 60		0.10		–	1.103
0.1	a = 8.270, c = 8.584	T	492		0 54		0 05		–	1.059
0.2	a = 8.340, c = 8 468	T	487		0 30		0 10		–	1.111
0.3	8 362	C	482		0.38		0 13		–	1.125
0 4	8 353	C	484	498	0 54	0 67	0.10	0 21	0.860	1 134
0.5	8.356	C	484	498	0 55	0 66	0.08	0 20	0 930	1 105
0 6	8.344	C	484	502	0 38	0 52	0 04	0 19	0 877	1.083
0.7	8.342	C	491	509	0 55	0 69	0 10	0 14	0.743	1 057
0.8	8 333	C	488	506	0 41	0 55	0 06	0 20	0 792	1 030
0 9	8 331	C	491	511	0 54	0 71	0 06	0 22	0 967	1 010
1 0	8 320	C	491	510	0 33	0 48	0 08	0 23	1 010	1 000

+—all values at 300 K , T—Tetragonal , C—Cubic ; †—from magnetisation data.

Results and Discussion

XRD patterns showed all the compositions as monophasic spinels. The compounds with x=0 0-0 3 were tetragonal and all other compositions were found to be cubic spinels, with lattice parameter decreasing linearly with increasing x

Mossbauer spectra are given in Fig 1 and the relevant parameters in Table 1 The spectra for the compositions x= 0-0 3 are of simple six-line type Although the lines are broad, they fitted well into six Lorentzians The large line width seems to suggest that the spectra may be due to superposition of two six-line patterns whose envelope is also Lorentzians For 0 4 ≤ x ≤ 1, the spectra no longer correspond to a single six-line pattern , the extreme line (in some cases, the last two or all the lines) on the positive velocity are split This is due to the superposition of two six-line patterns arising from Fe^{3+} ions at the two nonequivalent sites in the spinel structure This was first proposed by Evans *et al*[3] for $CuFe_2O_4$ who assigned the pattern with larger hyperfine splitting to the B site Fe^{3+} and that with the smaller hyperfine split to Fe^{3+} at A sites The same assignment may be accepted in the present case in view of the fact that isomer shift (IS) and quadrupole splitting (QS) of the latter are smaller It is possible to resolve the Lorentzians corresponding to Fe^{3+} at A and B sites and compute the relative concentrations of Fe^{3+} in the two sites The ratios of the areas under resonance I_B/I_A are given in Table 1 along with the ratio $[Fe^{3+}]_B/[Fe^{3+}]_A$ obtained from magnetisation values (Kiran *et al*[4]). It may be observed that the agreement between the two ratios is poor except for the compositions x = 0.9 and 1.0. Such discrepancy has also been reported by Evans and Hafner[1] who observed that for $CuFe_2O_4$ the intensity ratio was 0 6 and 0 7 for single crystal and ceramic samples, respectively, whereas expected cation ratio was between 1 22-1.33. Since the difference in recoilless fraction of Fe^{3+} at A and B sites is less than 10%, such large differences are unexpected. Since the assignment of the A and B sites appears to be correct, we along with Evans and Hafner[1] are forced to conclude that the discrepancy in the I_B/I_A values are due to anomalous line shapes brought about by different QS, IS and magnetic hyperfine fields (H_{eff}) at apparently equivalent sites Local symmetry at the 'Fe^{3+}_B' sites may be different depending upon the type and number of neighbouring cations. Distortions at these sites may be particularly important in copper containing ferrites because Cu^{2+} ions distort their environment severely. Symmetry of the iron site will then depend on the number of neighbouring Cu^{2+} ions which are randomly distributed Overall absorption lines may become non-Lorentzian in shape or may even split into a number of lines[1] The large line width may be
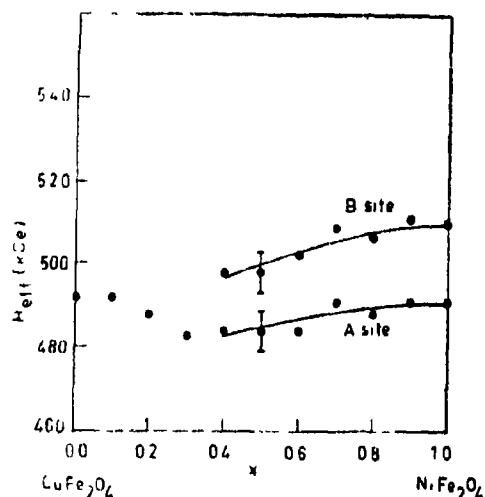
Fig. 2. Variation of hyperfine field (H_{eff}) with x in the system $Cu_{1-x}Ni_xFe_2O_4$.

suggestive of the presence of B site Fe^{3+} with different symmetry, although the overall spectra of B site iron fits into a set of Lorentzians.

The isomer shifts are all in the range 0.3-0.7 mm/sec with respect to $^{57}Co/Fe$ and this corresponds to iron in the trivalent state only. There is no regular variation of IS as well as of QS with composition.

The variation of the hyperfine fields at the A and B sites (H_{eff} average in case of $0 < x < 0.3$) with composition is given in Fig. 2 The hyperfine fields at both the sites increase with x. The relatively higher value of $H_{eff}(B)$ may be understood as follows. The average field for all the ions in a given sublattice is proportional to the average magnetisation of that sublattice. In an inverse ferrite, an Fe^{3+} ion at the B site will have all its nearest neighbouring A sites occupied by Fe^{3+} ions whereas the A site Fe^{3+} ion will have inter-sublattice bonds with Cu^{2+}, Fe^{3+} and Ni^{2+}. Since Fe_A^{3+}-O^{2-}-Fe_B^{3+} is the strongest superexchange interaction, the H_{eff} of an Fe^{3+} ion surrounded in part by cations other than Fe^{3+} will be smaller than when surrounded by all Fe^{3+} ions only. The increase in H_{eff} at A sites as x increases could be due to the fact that the interaction Fe_A^{3+}-O^{2-}-Ni_B^{2+} is stronger than Fe_A^{3+}-O^{2-}-Cu_B^{2+}. The increase in $H_{eff}(B)$ with x is due to the fact that as x increases from 0.4 onwards, the fraction of A sites occupied by the Fe^{3+} ions also increases as shown by the magnetisation data, and hence the number of Cu^{2+} ions on A sites decreases in these compositions[6].

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Cyclic Voltammetry of Thallium(I) in Different Supporting Electrolytes

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The reduction of Tl(I) has been made in presence of various sodium salts as supporting electrolytes at a hanging mercury drop electrode (HMDE) The correlation of cathodic and anodic peak currents and the difference in cathodic and anodic peak potentials with the voltage scan rates indicate that the reduction of Tl(I) is not reversible.

WITH the help of the theory of stationary electrode voltammetry proposed by Nicholson and Shain[1], it is possible to develope diagnostic criteria by correlating kinetic and experimental parameters so that unknown system can be characterized by studying the variations of peak current, half-peak potential, or ratio of anodic to cathodic peak currents as a function of rate of voltage scan

For a reversible system the separation of peak anodic and cathodic potentials of the couple[2] is $\frac{58}{n}$ mv and to a good approximation the formal electrode potential can be computed by averaging the two peak potentials. However, the peak to peak distance is larger for an irreversible system[3]

The effect of a chemical reaction on the voltammetric wave will depend on its rate, as compared with the time required to perform the experiment. Taking irreversible succeeding chemical reaction as an example, if a very rapid reaction is studied with very slow scan rates, the stationary electrode voltammogram will reflect the characteristics of the chemical step almost entirely On the other hand, if the rate of voltage scan is rapid compared to the rate of the reaction, the curves are identical to those for the corresponding uncomplicated charge transfer reactions Hence in every kinetic case, the ratio of the rate constant to the rate of voltage scan appears in the kinetic parameter. This, in turn, makes it possible to use these relations to define diagnostic criteria for the investigation of unknown systems.

The relationship between scan rate (V) and I_{pa}/I_{pc} or $I_{pc}/V^{1/2}$ is often used as a diagonistic criteria for identifying the nature of the electrode process. Here I_{pa} and I_{pc} are anodic and cathodic peak currents in a cyclic voltammogram.

The authors have used these criteria to investigate the reduction of Tl(I) in different supporting electrolytes

Experimental

Cyclic voltammograph CV-1, (Bioanalytical System Inc., U S A), in combination with an X-Y recorder (Digilog) was used to record the cyclic voltammograms

A special cell having three-electrode assembly was used Hanging mercury drop electrode (HMDE)[4-7] was used as the working electrode while a platinum spiral was employed as the auxiliary electrode. All potentials were measured against a saturated calomel electrode (SCE) which was connected to the test solution through a sodium nitrate bridge All experiments were carried out at 35±0 1° by immersing the cell and the reference electrode in a cryostat, type MK-70 (Web Mlw Prufgerate Werk, GDR).

Reagent grade chemicals were used in all the experiments The concentration of Tl(I) ion was kept at 5×10^{-4} *M*, while the supporting electrolytes used were $NaNO_3$, $NaClO_4$, NaCl and Na_2SO_4.

Cyclic voltammograms were taken at different scan rates varying from 0.02 to 0.1 volt/sec. The

TABLE 1—POTENTIAL VALUES OF Tl^+ IN DIFFERENT SUPPORTING ELECTROLYTES (IN VOLTS VS SCE)

Sl. No.	Scan rate Volts/sec	0.1 *M* $NaNO_3$			0.1 *M* NaCl			0.1 *M* $NaClO_4$			0.1 *M* Na_2SO_4		
		E_{pa}	E_{pc}	ΔE_p	E_{pa}	E_{pc}	ΔE_p	E_{pa}	E_{pc}	ΔE_p	E_{pa}	E_{pc}	ΔE_p
1.	0.02	−0.47	−0.55	0.08	−0.48	−0.56	0.08	−0.47	−0.55	0.08	−0.49	−0.57	0.08
2	0.03	−0.47	−0.55	0.08	−0.48	−0.55	0.07	−0.47	−0.55	0.08	−0.49	−0.57	0.08
3.	0.04	−0.47	−0.55	0.08	−0.47	−0.55	0.08	−0.47	−0.55	0.08	−0.49	−0.57	0.08
4.	0.05	−0.46	−0.55	0.09	−0.47	−0.55	0.08	−0.47	−0.54	0.07	−0.49	−0.57	0.08
5.	0.06	−0.46	−0.55	0.09	−0.47	−0.55	0.08	−0.47	−0.55	0.08	−0.48	−0.56	0.08
6.	0.07	−0.46	−0.55	0.09	−0.47	−0.55	0.08	−0.46	−0.54	0.08	−0.49	−0.57	0.08
7.	0.08	−0.46	−0.56	0.10	−0.47	−0.54	0.08	−0.47	−0.55	0.08	−0.49	−0.57	0.08
8.	0.09	−0.46	−0.56	0.10	−0.47	−0.55	0.08	−0.46	−0.55	0.09	−0.48	−0.56	0.08
9.	0.10	−0.45	−0.55	0.10	−0.46	−0.54	0.08	−0.46	−0.54	0.08	−0.49	−0.57	0.08

TABLE 2—VALUES OF CATHODIC AND ANODIC PEAK CURRENTS IN MICROAMPERES

Sl. No.	Scan rate Volts/sec.	0 1 *M* $NaNO_3$			0.1 *M* NaCl			0.1 *M* $NaClO_4$			0.1 *M* Na_2SO_4		
		I_{pa}	I_{pc}	I_{pa}/I_{pc}	I_{pa}	I_{pc}	I_{pa}/I_{pc}	I_{pa}	I_{pc}	I_{pa}/I_{pc}	I_{pa}	I_{pc}	I_{pa}/I_{pc}
1.	0.02	5.05	2.45	2 06	4.75	2 0	2.38	4.50	1.85	2 43	2 6	1 5	1.73
2.	0.03	5 6	3.4	1.64	5.0	2.8	1.79	4.7	2 65	1.74	3.05	1 9	1.6
3.	0.04	6.05	3 95	1.53	5.3	3.25	1.63	5 05	2 8	1.8	3.3	2 2	1.5
4.	0 05	6.0	4 05	1 48	5 45	3 45	1.58	5 05	3 3	1.53	3.5	2 5	1.4
5.	0.06	6 4	4 3	1.49	5.5	3.7	1.49	5.25	3.65	1 44	3 35	2 65	1.26
6.	0.07	6.75	4.95	1.57	5.75	4.05	1.42	5 65	4 0	1 41	3.85	2 8	1.37
7.	0 08	6.85	4.5	1.52	5 55	3.85	1.44	5.3	3 85	1.38	4 0	3.0	1.33
8.	0.09	7.5	5 4	1.5	5.90	4.35	1 36	5.8	4.35	1.33	4.1	3.25	1 26
9.	0.10	8.05	5.75	1.4	6.1	4 5	1.36	5.8	4.3	1 35	4.2	3 4	1.24
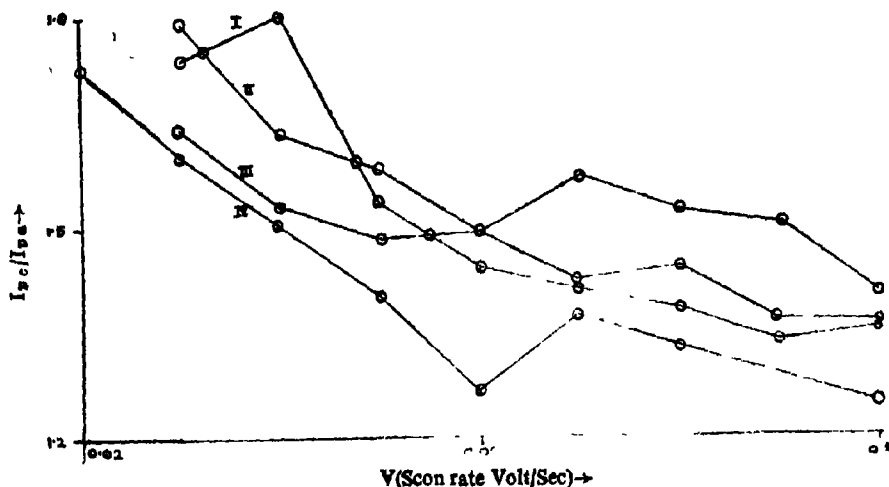
Fig. 1. Plot of I_{pa}/I_{pc} vs scan rate (V) in different supporting electrolytes : (I) 0.1*M* $NaClO_4$; (II) 0.1*M* NaCl ; (III) 0 1*M* $NaNO_3$; (IV) 0.1*M* Na_2SO_4.
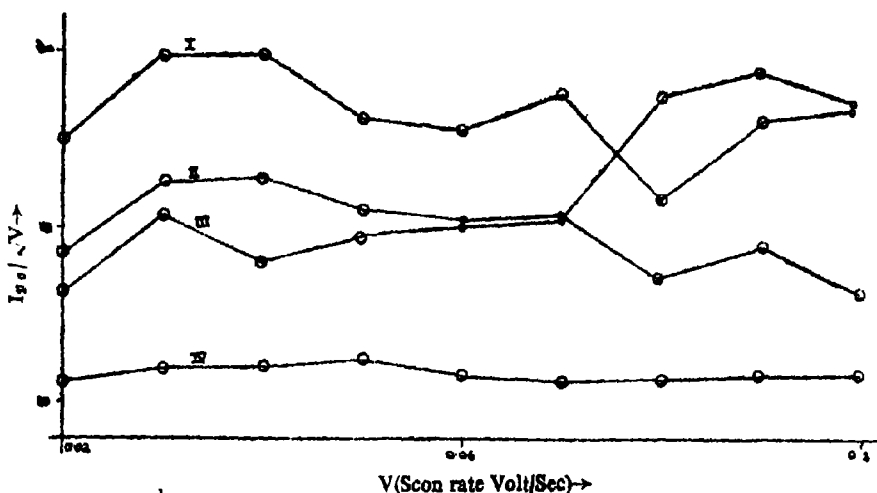
Fig. 2. Plot of $I_{pa}/V^{\frac{1}{2}}$ vs scan rate (V) in different supporting electrolytes : (I) 0.1*M* $NaNO_3$; (II) 0.1*M* NaCl , (III) 0 1*M* $NaClO_4$, (IV) 0.1*M* Na_2SO_4

starting and returning potentials were —0.2 and —1 0 volt, respectively.

Results and Discussion

The anodic and cathodic peak potentials (E_{pa} and E_{pc}) and peaks potential differences (ΔE_p) were calculated from the cyclic voltammograms obtained in different supporting electrolytes (Table 1).

One of the criteria for reversibility is that $\Delta E_p = \frac{58}{n}$ mv. It is clear from Table 1 that the reduction of Tl(I) is not reversible in any of the supporting electrolytes, since $\Delta E_p \approx 0.08$ volt in all the cases. It is further noted that ΔE_p remains unchanged on increasing the scan rate. However, the values of E_{pa} and E_{pc} are more negative in 0.1 *M* Na_2SO_4 supporting electrolyte.

The cathodic and anodic peak currents were measured at different scan rates for various supporting electrolytes. Results are given in Table 2 in which the values of I_{pa}/I_{pc} are also recorded. It is seen that the ratio I_{pa}/I_{pc} is not unity in any case. On increasing the scan rate, the ratio decreases regularly due to the fact that the cathodic peak current is enhanced at high scan rates. The plot of I_{pa}/I_{pc} vs V is shown in Fig. 1

TABLE 3

Sl No	Scan rate Volts/sec V	0 1 *M* $NaNO_3$ $I_{pc}/V^{\frac{1}{2}}$	0 1 *M* NaCl $I_{pc}/V^{\frac{1}{2}}$	0.1 *M* $NaClO_4$ $I_{pc}/V^{\frac{1}{2}}$	0.1 *M* Na_2SO_4 $I_{pc}/V^{\frac{1}{2}}$
1.	0 02	17.4	14.2	13 1	10 6
2.	0.03	19 7	16 2	15 3	11.0
3.	0.04	19 8	16 3	14.0	11 0
4	0 05	18 1	15 4	14 7	11.2
5	0 06	17 6	15 1	14.9	10 8
6	0 07	18 7	15 3	15 1	10 6
7.	0 08	15.9	13 6	18 7	10.6
8	0 09	18.0	14 5	19 3	10.8
9	0 10	18 2	14 2	18.4	10.8

The ratios of cathodic peak current and square root of scan rate, for different supporting electrolytes, are given in Table 3. The plots of $I_{pc}/V^{\frac{1}{2}}$ vs V for all the supporting electrolytes are given in Fig. 2. The plots yield almost horizontal lines.

All the above mentioned data indicate conclusively that the reduction of Tl(I) in the supporting electrolytes employed is not reversible at a mercury electrode This conclusion appears contradictory to the accepted notion that the polarographic reduction of Tl(I) is reversible[8]. This clearly shows that the criteria of reversibility based on logarthmic plot analysis of polarographic curves is not reliable.

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Hydrogen Ion Equilibria and Metal Binding Studies on Arachin

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Arachin, a protein with molecular weight 3,30,000, was isolated from defatted ground nut powder and purified to homogenity Hydrogen ion equilibrium studies were carried out and the number of binding sites in the protein molecule was calculated which were confirmed by calculating heat of ionization (H_{ion}) on the basis of pH measurements at three different temp. The work also reports polarographic investigation of complexes formed by copper and zinc metal ions with arachin in the higher pH range. The results show that the amino groups of arachin bind copper ions more strongly than carboxyl groups.

IN view of its important contribution to the knowledge of molecular structures of proteins and their interaction with the environment, the hydrogen ion equilibrium of protein has been studied by a number of workers[1-7]. The present communication deals with the studies on hydrogen ion equilibria of arachin, which is isolated from ground nuts The protein is edible and literature survey indicates no such studies on it

The work also includes polarographic investigation of complexes formed by copper and zinc ions with arachin, in the higher pH range. Some of the results in the lower pH range have also been included but the binding is too weak to give useful quantitative results.

Experimental

Isolation of arachin :

Ground nuts (1 kg) were crushed finely and extracted with petroleum ether (40-60°) The defatted ground nut powder was dried in air, dipped in sodium chloride solution (10% ; 500 ml) overnight and filtered. Ammonium sulphate (A R) was added in the filtrate upto 0 2 saturation, when a white precipitate of arachin was obtained. It was filtered, washed free from salts and dried in vacuum (5 g). Further addition upto 0 8 saturation resulted in another white precipitate, which was of conarchin. The homogenity of arachin was confirmed by circular paper chromatography using NaCl (10%) as the developing solvent and Solway purple (0.5%) containing H_2SO_4 (0.5%) at 60°-70°, as the locating reagent. The chromatogram showed a single violet coloured patch for arachin only The amino acid assay further confirmed the purity of arachin. Thus, the molecular weight of arachin was taken to be 3,30,000.

Apparatus and technique :

pH meter (expanded scale) was used. The instrument was standardised with standard solution of potassium hydrogen phthalate (pH 4.12) and borax buffer (pH 10).

Reagents and solutions[8] .

A 4 8% solution of arachin was used. Solutions of HCl, KOH (carbonate free), KCl (all AR) were prepared with double distilled water in all glass apparatus.

Procedure

Varying amounts of HCl, (26 04, 17 95, 13 06, 8 34, 6 49, 3 72 and $1.82\times10^{-3}M$) and KOH (2 314, 4 629, 6 943, 13.887 and $23.145\times10^{-3}M$) were taken in 50 ml pyrex conical flasks and 2 ml of arachin solution was added to each of them. The total volume was made upto 10 ml by the addition of requisite amount of 1 *M* KCl (μ=0.15) and water.

TABLE 1—pH MEASUREMENT RESULTS (WITH ACID)

Temp 24°, ionic strength 0.15, conc of arachin 4 8 g/l

H^+ added (Moles/ 1 10³)	pH	Free H^+ (Moles/ 1 10³)	Bound H^+ (Moles/mole protein)	Moles of H^+ dissociated per mole protein
26 04	1 7	19 95	420	0
17 09	2 0	10.00	488	0
13.06	2 1	7.94	353	67
8 34	2 3	5.011	229.1	190.9
6.49	2 4	3 981	173.1	246.8
3 72	2 6	2.512	83 45	336 5
1.82	3 0	1 0	56 55	363 45
0.00	6 5	0.0003	0	420

pH MEASUREMENT RESULTS (WITH ALKALI)

Temp. 24°, ionic strength 0 15, conc. of arachin 4.8 g/l

OH^- added (Moles/ 1.10³)	pH	Free OH^- (Moles/ 1.10³)	Bound OH^- (Moles/mole protein)	Moles of H^+ dissociated per mole protein
2.314	8.3	0 0019	159 2	579.2
4.629	10.2	0.15	308.2	728.2
6.924	11.3	1.99	341.58	761.58
13.887	11.9	7.9	412.4	832.4
23.14	12.25	17.78	369.65	789.65

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TABLE 2—pH MEASUREMENT RESULTS (WITH ACID)

Temp. 30°, ionic strength 0 15, conc. of Arachin 4 8 g/l

H^+ added (Moles/ 1.10^{8})	pH	Free H^+ (Moles/ 1.10^{8})	Bound H^+ (Moles/mole protein)	Moles of H^+ dissociated per mole protein
26.04	1 7	19 95	420	0
17.09	1.95	11.22	411 7	8 3
13 06	2.1	7 9	353	67
8.35	2 3	5 01	229 1	190 9
6.49	2.54	2.88	248 9	171.1
3.72	2 75	1 77	134 48	285 52
1.82	3.0	0 794	70 75	394 25
0.00	6 6	0 0002	0	420

pH MEASUREMENT RESULTS (WITH ALKALI)

Temp 30°, ionic strength 0.15, conc of arachin 4 8 g/l

OH^- added (Moles/ $1\ 10^{8}$)	pH	Free OH^- (Moles/ $1\ 10^{8}$)	Bound OH^- (Moles/mole protein)	Moles of H^+ dissociated per mole protein
2 314	8.1	0013	159 3	579 3
4.629	9 9	079	313 7	733 7
6 943	11.2	1 58	369 7	789 7
13 887	11 8	6 30	523 24	943 24
23 145	12 25	17 78	369 65	789 65

TABLE 3—pH MEASUREMENT RESULTS (WITH ACID)

Temp. 40°, ionic strength 0 15, conc. of arachin 4 8 g/l

H^+ added (Moles/ $1\ 10^{8}$)	pH	Free H^+ (Moles/ 1.10^{8})	Bound H^+ (Moles/mole protein)	Moles of H^+ dissociated per mole protein
26.04	1.69	20 02	415.2	0
17 95	2 0	10 98	414	6 0
13 06	2 1	7.94	353	67
8 34	2 3	5.012	229 1	190.9
6.49	2 4	3 981	173.2	246 8
3.72	2.59	2.57	79.2	340.8
1.82	3 0	1.0	56 55	363.45
0,00	6 5	0 0002	0	420

pH MEASUREMENT RESULTS (WITH ALKALI)

Temp. 40°, ionic strength 0.15, conc. of arachin 4.8 g/l

OH^- added (Moles/ 1.10^{8})	pH	Free OH^- (Moles/ 1.10^{8})	Bound OH^- (Moles/mole protein)	Moles of H^+ dissociated per mole protein
2 314	8 3	0 0019	159 2	519 2
4.629	9 9	0.079	305 5	725.5
6.943	11.2	1 99	341.58	761 58
13.887	11.9	7.99	412 3	832 3
23.145	12.26	17 0	420 0	840

The pH measurements were carried out at three different temp viz., 24, 30 and 40° by keeping the cell in a water thermostat. Typical results are recorded in Tables 1 to 3 and are graphically represented (Fig. 1).

Calculation :

The number of equivalent of H^+ ions which are bound when a protein is brought from the isoionic conditions to a state in which all dissociable groups have assumed their acidic forms is equal to the number of cationic acid groups in the molecule while the equivalent of hydrogen ion dissociated between the isoionic and fully basic state of protein are equal to the number of anionic basic groups[8].
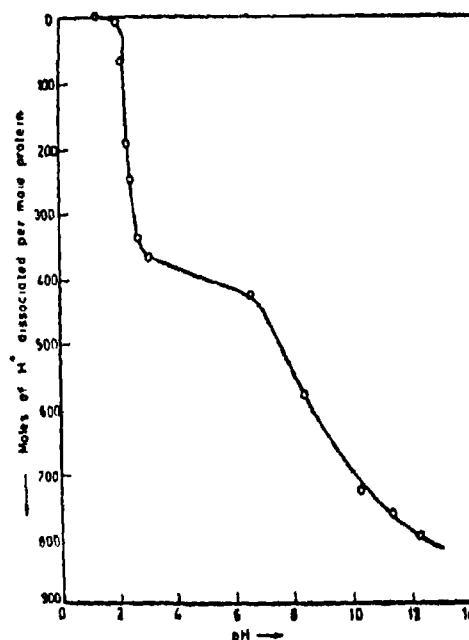
Fig 1 Titration curve of arachin at 24°, ionic strength 0.15.

The apparent heat of ionization (ΔH_{ion}) was determined according to Wyman's method[10] using the equation

$$H_{ion} = -2.303\ RT^2 \left(\frac{dpH}{dt}\right)$$

The apparent heat of ionization, ΔH_{ion}, was plotted against the number of protons dissociated per protein molecule (Fig 2).
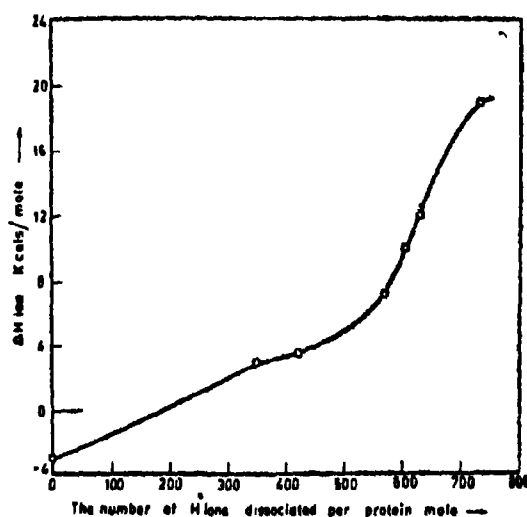
Fig. 2. The relation between the apparent heat of ionization and the number of protons dissociated per protein molecule.

Discussion

The titration curve (Fig. 1) consisted of three main parts corresponding to the groups which titrate in the acid, neutral and alkaline regions.

The titration curve approached a limiting value of hydrogen ions bound at pH 2 where all carboxyl groups were in their acidic form. The pH 6.5 indicates that all carboxylic groups were in their basic forms. Thus the total number of carboxyl group is 420. It was interesting to note that the carboxyl region showed again a break at pH 3.2, since no other titrable groups except glutamic and aspartic acid, are expected[11]. The portion between pH 2 to 3 2 corresponded to aspartic acid residue (360) and that between 3.2 to 6.5 corresponded to glutamic acid (60) residue. These values were in agreement with those obtained from arachin assay[12] giving the value of 347 and 65 for aspartic and glutamic acid, respectively.

The second part of the titration curve from pH 6.5 to 8 corresponded to neutral region indicating the dissociation of imidazolium groups of histidine. The number of imidazolium groups is 130, which is a bit higher than that obtained from assay. This is perhaps due to the fact that

(1) the maximum hydrogen ion binding capacity includes also the contribution of an uncertain fraction of the histidine residue,

(2) the dissociations are not easily distinguishable from those of the phenoxyl group of tyrosine and sulphydryl group of cystine, since they occur in overlapping range of pH, and

(3) the titration with base is generally incomplete.

The third main part of the titration curve from pH 8 to 12 indicates the number of basic groups to be 230 It includes mainly lysine and arginine with side chain amino groups, with a contribution from phenolic, sulphydryl, ammonium and guanidinium groups.

The plot of apparent heat of ionization $\triangle H_{ion}$ against the number of proteins dissociated per protein molecule (Fig. 2) shows the expected range[b,11] of ionizable groups in arachin and lends support to the above results.

Copper and zinc metal binding studies with polarography :

The manual polarograph was used. A H-shaped polarographic cell was found suitable for deaeration of protein solution without denaturation. Nitrogen gas (purified) was passed for about 15 to 20 min to ensure an inert atmosphere. Triply distilled mercury (A R.) was used for dropping mercury electrode The capillary used had a flow rate of about 2.2 mg/sec with a drop time of 3.5 sec.

Since the capillary characteristics (m, t) have a marked effect on diffusion current (which is directly proportional to $m^{2/3} t^{1/6}$), these factors were controlled carefully throughout these experiments.

The pH of the buffers and mixture of metal and protein solutions were measured by pH meter using a wide range glass electrode.
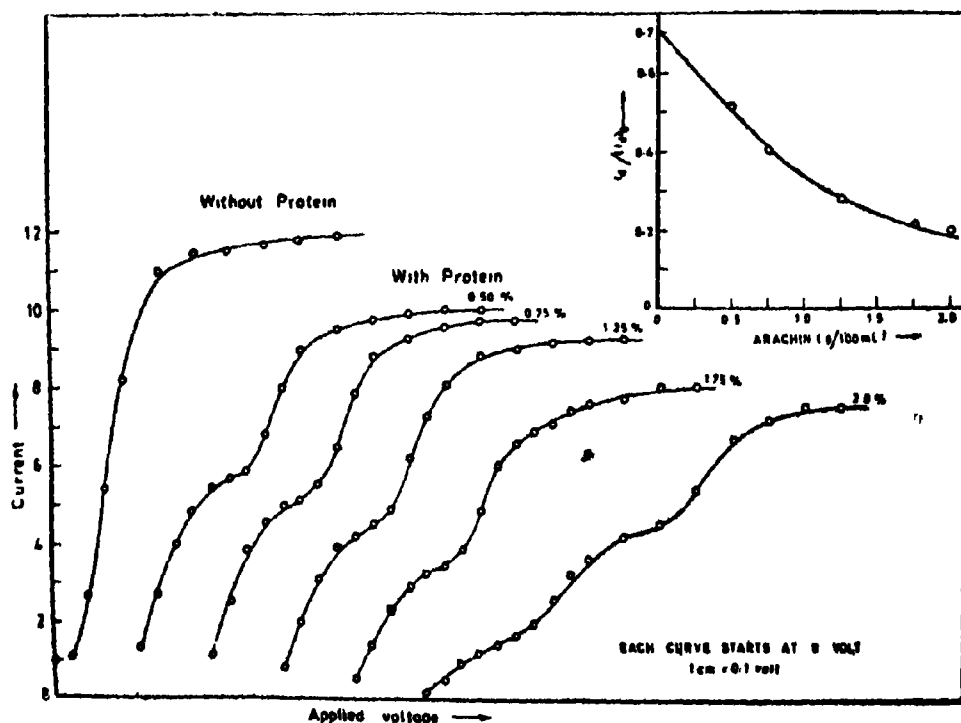
Fig. 3. Effect of protein concentration on diffusion current.

Reagents and solutions :

Solution of arachin was prepared by dissolving it in double distilled water. Copper sulphate and zinc sulphate (A.R.) were dissolved in double distilled water. Ammonia-ammonium chloride buffers were prepared from 1 0 *M* solutions of ammonia and ammonium chloride.

Procedure :

The following sets of solution were prepared for polarographic analysis :

(1) Varying concentration of the protein (0 5, 0 75, 1.25, 1.75 and 2%) were taken in 50 ml conical flasks and 4.5 ml of 0 005*M* Cu^{2+} solution added. The total volume was made upto 12 ml by adding the requisite volume of water and 1.8 ml of 1*M* ammonia-ammonium chloride buffer (μ=0.15). The results, in the form of a graph of protein concentration (%) against $(i_d)/(i_d)_o$, where i_d and i_{d_0} are the diffusion currents of the metal ion, in the presence and absence of the protein, respectively, are shown in Fig. 3.

Table 4—Conc of Cu^{++}, 1 87 × 10^{-3} *M*, *p*H 9.4

Conc. of protein (%)	i_d	$(i_d)_o$	$i_d/(i_d)_o$	C_b	V_M
0 50	4 6	9	0.51	1.14	76
0 75	3.6	9	0 40	1.37	62.2
1.25	2 5	9	0.28	1 67	42 4
1 75	2 0	9	0 22	1 82	34.3
2 00	1 8	9	0.20	1.86	31.0
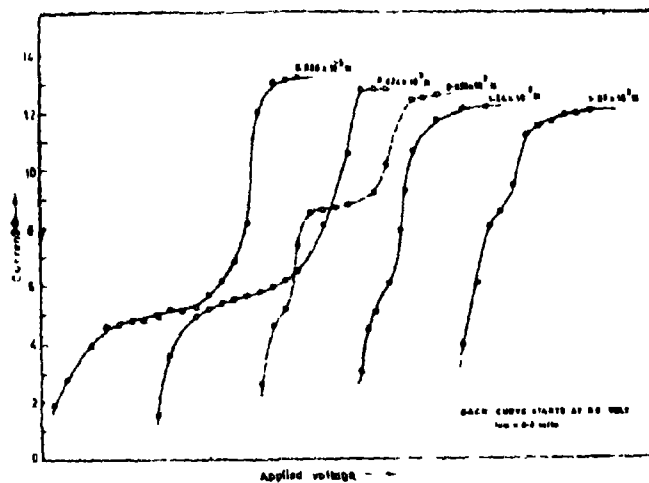
Fig. 4. Effect of copper concentration on diffusion current depression (without protein)
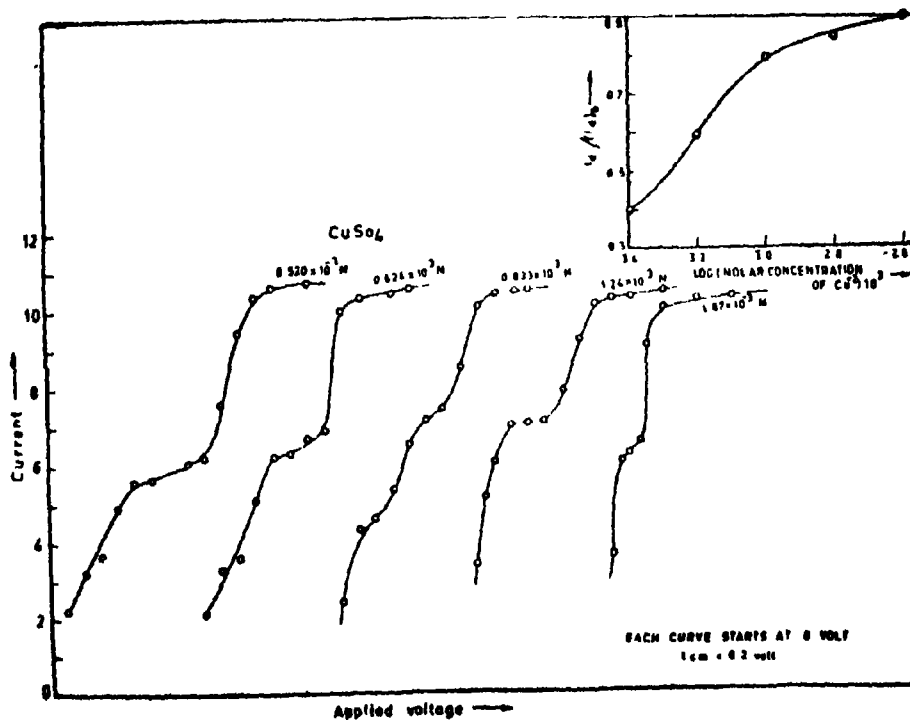
Fig. 4.1. Effect of copper concentration on diffusion current depression.

(2) 1 ml arachin, 1.8 ml buffer (*p*H 9.4) and varying concentration of Cu^{2+} ion, viz. 0.4166, 0.6249, 0.8332, 1 249 and 1.874×10^{-3} *M* Cu^{2+} were used, keeping the total volume to 12 ml as before. Similar sets without protein were also prepared (Figs. 4 and 4.1)

TABLE 5—CONC. OF THE PROTEIN, 0 5%

Conc. of $Cu^{2+} \times 10^{-3}$ *M*	i_d	$(i_d)_0$	$i_d/(i_d)_0$	C_b	V_M
0.520	2.2	1 8	0 4	0.520	34 6
0.624	2 8	2 3	0 6	0.416	27.4
0 833	3 3	2 7	0 8	0 277	18.4
1 24	4 8	3 0	0 85	0 31	20.6
1.87	6 9	3 3	0.9	0.311	20.6

(3) Similarly, at a given concentration of copper sulphate ($0.624 \times 10^{-3} M$) and the protein (0.5%), ammonium buffers of varying *p*H, viz 11, 10, 9, 4, 6.1 and 2 6 were taken making the total volume 12 ml by the addition of water. The ionic strength was thus maintained at 0.15. Similar sets without protein was also prepared (Figs. 5 and 5.1).

(4) (i) At *p*H 9.6, varying concentration of zinc sulphate, viz 3.33, 5.66 and $8 9 \times 10^{-4} M$ were taken with 2.5% protein in pyrex conical flasks Another similar set without protein was also prepared The total volume was made upto 15 ml with water and potassium chloride (to make ionic strength 0 15) solution (Fig 6).
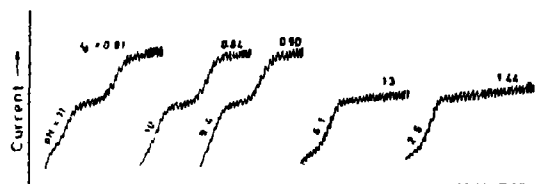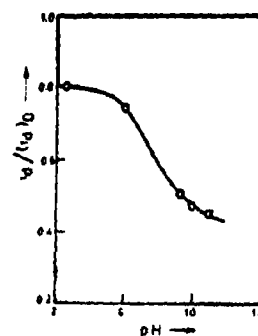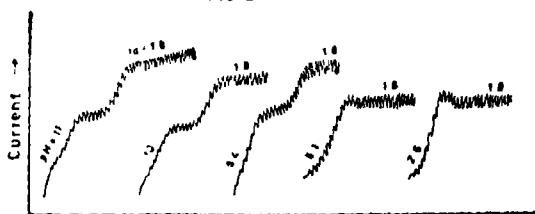
Fig 5.1. Effect of *p*H on diffusion current depression.
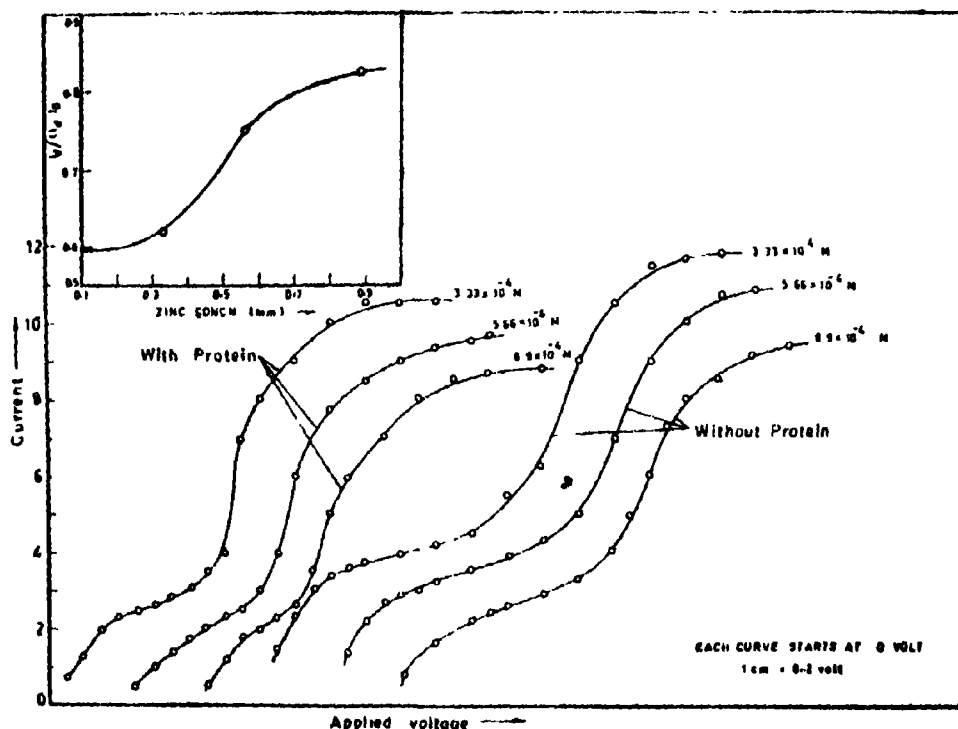
Fig. 6. Effect of zinc concentration on diffusion current depression.

TABLE 6—CONC. OF THE PROTEIN 0.5%, CONC OF Cu^{2+}624 × 10^{-6}

pH	i_d	$(i_d)_0$	$i_d/(i_d)_0$	C_b	V_M
11	0.81	1.8	0 45	0 624	41 6
10	0.84	1.8	0 47	0.601	40 7
9.4	1.9	1.8	0 5	0 567	37 8
6.1	1.3	1.8	0.74	0 294	19.6
3.6	1.44	1.8	0 8	0 226	15 0

(ii) Similarly, 1.5 ml of 8.33 × $10^{-4}M$ Zn^{2+} solution, 1 ml protein and 1.8 ml buffer of different pHs from pH 2.6-11 were taken and the volume was made upto 15 ml by adding water and potassium chloride Similar sets without protein were also prepared (Figs. 7 and 7.1).

TABLE 7—CONC. OF THE PROTEIN 2.5%, pH 9.4

Conc. of Zn^{2+} × $10^{-4}M$	i_d	$(i_d)_0$	$i_d/(i_d)_0$	C_b	V_M
0 89	5 1	8 0	0.62	0.845	10.5
0 56	4 7	6 4	0.75	0 35	4.3
0 33	3 9	4 7	0 82	0.148	1.8
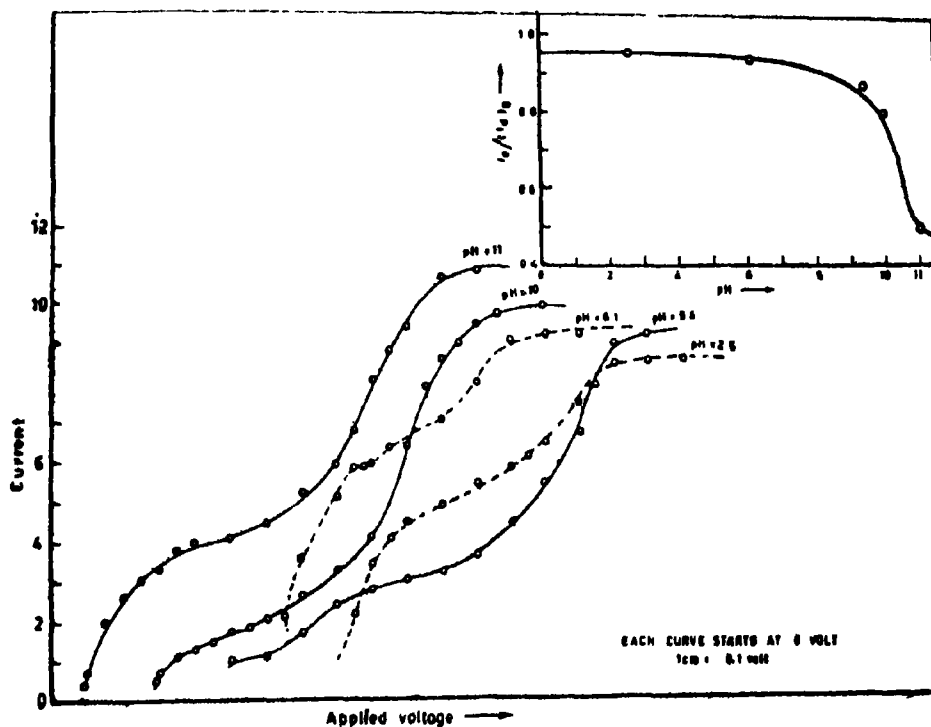
Fig. 7. Effect of pH on diffusion current depression (with protein).
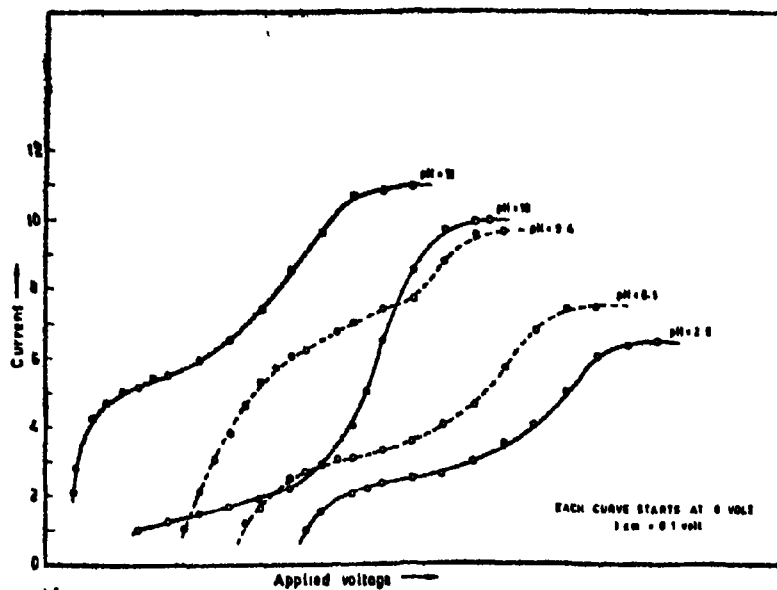
Fig. 7.1. Effect of pH on diffusion current depression (without protein).

TABLE 8—CONC. OF THE PROTEIN 2 5%, CONC. OF Zn^{2+} 8.33 x 10^{-4} *M*

pH.	i_d	$(i_d)_0$	$i_d/(i_d)_0$	C_b	V_M
11	6 2	3.3	0 5	0 833	10.4
10	4 3	3.2	0.8	0 333	4.1
9 4	3.2	2.9	0.87	0 216	2 7
6.1	2.5	2.2	0 94	0.099	1 2
2.6	2.1	1.8	0.95	0 083	1 0

(iii) Varying concentrations of the proteins (0.5, 1.2, 2.0, 2.3 and 2.5%) were taken in 50 ml conical flasks and 4 5 ml of $8.33\times10^{-4}M$ Zn^{2+} solution were added. The total volume was made upto 15 ml by adding water and potassium chloride (Fig 8).
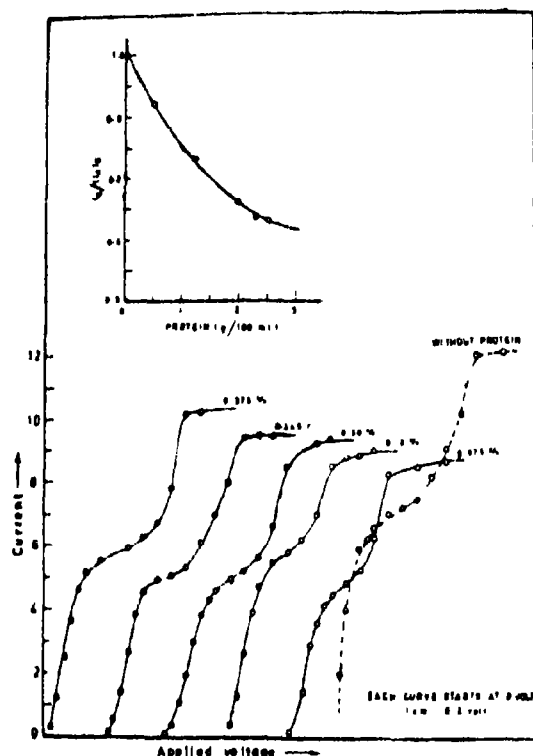
Fig 8. Effect of protein conc. on diffusion current.

TABLE 9—CONC OF Zn^{2+} 8 33 x 10^{-4} *M*, *p*H 9.4

Conc of protein (%)	i_d	$(i_d)_0$	$i_d/(i_d)_0$	C_b	V_M
0.5	6 1	3 5	0 55	0 833	35
1 2	6 1	3 6	0 57	0 795	19 8
2.0	6 1	3 7	0 61	0 721	12.0
2.3	6 1	4 6	0 76	0 444	6 3
2.5	6.1	5 7	0 94	0.111	1 3

Discussion

The usual polarographic method for the study of metal complexes from the shift in half wave potential of the metal ion[18] failed to give precise information regarding the metal protein interaction because of very small variations in $E_{1/2}$ values of the order of 0.01 V. Tanford's method[14,15], with all its limitations, could however be advantageously employed. Since the copper arachin complex (blue in colour) and zinc arachin complex are formed only at higher *p*H ranges, the adsorption effects usually encountered could be assumed to exert the minimum influence and the decrease in the ratio $i_d/(i_d)_0$ can be safely taken as a measure of the extent of metal ion complexed with the protein.

The decrease in the $i_d/(i_d)_0$ values at *p*H 9.4, determined experimentally, provides enough information regarding the binding of Cu^{2+} and Zn^{2+} with arachin. From Tanford's equation

$$\frac{i_d}{(i_d)_0} = \frac{C+KC_b}{C_0},$$

where C and C_b are the conc. of free and bound copper or zinc, C_0 its total concentration and K a constant which can be evaluated from the limiting values of i_d [K for set (a) is 0.2], the amount of bound copper can be found. The amount of bound zinc can also be obtained similarly. Taking the molecular weight of arachin to be 33,000. the amount of metal bound (V_M) per mole of the protein could be determined. The results are summarised in Tables 4-9. From these, the values of V_M is seen to be approximately 34 at *p*H 9.4 for Cu^{2+} whereas for Zn^{2+} the value of V_M is 10 at *p*H 9.4.

Polarographic measurements carried out at different *p*H values show that the value of V_M ranges between 37-41.6 for the *p*H range 8.9-11, while at lower *p*H, V_M ranges between 15-19.6. These results are significant since they show that the amino groups of arachin bind copper ions more strongly than carboxyl groups

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Metal-Polyalkoxylate Complexes and their Applications in Analytical Potentiometry

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The complexation of polyalkoxylates with metals is discussed and preparation of tetraphenyl borates of the complexes summarized. The most appropriate methods for analyzing alkoxylates are based on their complexation reactions with metals in gravimetric, titrimetric and spectrophotometric procedures Such reactions and the equilibrium between complexed metals and alkoxylates form the basis of membrane electrodes responding to various cations, especially with barium, lead and calcium ion selectivity, and to alkoxylates themselves. Among the applications for the barium and lead ion-selective electrodes are their use as endpoint indicators in the potentiometric titration of sulphate The responses of the electrodes for polyalkoxylates may be used for evaluating critical micelle concentrations (CMCs) and analysis for these categories of non-ionic surfactants

STRONG stoichiometric complexes of metal ions with neutral molecules have been observed only in recent years, the main interest being with biological materials and macrocyclic polyethers The essential complexing principle is that these neutral organic molecules carry a sequence of localised charges (usually lone-pair electrons) of sufficient energy to form ion-dipole ligands with appropriate cations. The conformation of the molecule is such that it forms a solvation type shell around the cation, effectively replacing the ion hydration shell. The charged cationic complex thus formed is electrically balanced by anions.

Apart from the macrocyclic types of polyethers, there are the acyclic polyalkoxylates whose complexing tendencies with various cations and associated analytical connotations have been much studied in the author's laboratories and by others. It is appropriate, therefore, that fulfilment of the privileged invitation to contribute a paper for this Commemoration Volume in honour of the 60th birthday of Professor Arun K. Dey, should centre on these complexes, especially in view of the tremendous current interest in analytical chemistry circles of the whole field of complexation between metal ions and neutral molecules.

Nature of metal:alkoxylate complexes :

Polyalkoxylates are essentially acyclic polyethers with the $-(\underset{\displaystyle R}{\underset{|}{C}}HCH_2O)-$ repeating unit They include polyethylene glycols (PEGs) $[HO(CH_2CH_2O)_nH]$, polyglycol dimethyl ethers (glymes)$[CH_3O\cdot(CH_2CH_2O)_nCH_3]$, polypropylene glycols (PPGs) $[HO(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2O)_nH]$, and alkylphenoxypolyethoxylates of which the nonylphenoxypolyethoxylates(NPs) $[C_9H_{19}C_6H_4O(CH_2CH_2O)_nH]$ are typical.

The materials have various applications. For example, the low molecular mass PEGs are solvents, while the NPs are important non-ionic surfactants and variation in the number of ethoxylate units can produce useful changes in wetting, detergency, emulsification, solubility and foam properties,

It is appropriate to note the evolution of an understanding of the nature of these complexes. The polyelectrolyte properties of polyalkoxylates in the presence of metal ions suggested an association, as was confirmed by nmr studies of ion-dipole interactions between potassium iodide and polyethoxylate[1]. Such interactions were, of course, evident from procedures for the analysis of alkoxylates Also, there were the reaction between potassium alcholate and polyalkoxylates[2] ; spectrophotometric data on polyalkoxylates in the presence of sodium, potassium, and ammonium thiocyanates[3]; X-ray diffraction and other studies of complexes of mercury(II) halides with polyethoxylate[4,5] and related ethoxylate oligomers[6] ; and also the temperature-dependent optical and nmr spectroscopic data on the effectiveness of glymes as coordinating agents for alkali metal ions and for the ion pairs of flurenyl carbonium alkali metal ion salts[7,8].

The tetraphenylborate salts of complexes between the NPs and other alkoxylates and alkaline earth and other metal cations, especially barium, have been exploited for their response in membrane electrode potentiometry[9-24]. This has led to rather direct interest in synthesising salts of the complexes.

Of the several methods for obtaining polyalkoxylate adducts, the conversion with tetraphenylborate ions is very convenient and an extended range of the tetraphenylborates of cation complexes with PEGs, PPGs and NPs has been prepared in the author's laboratories. These are summarised in Table 1.

The preparative method is simple and straightforward[15,25,26] and merely involves adding an

TABLE 1—TETRAPHENYLBORATES OF METAL CATION ADDUCTS OF POLYALKOXYLATES[25,26]

Polyalkoxylate	No. of AOUs	Stoichiometry of TPB precipitate	No. of AOU per cation	m.p.[a] °C
Antarox CO-880	30	$Na(CO\text{-}880)_{0.28}.TPB$	8.4	98–100
		$Mg(CO\text{-}880)_{0.4}.TPB_2$	12.0	40–45 with decomposition
		$Ca(CO\text{-}880)_{0.4}.TPB_2$	12.0	185–190
		$Sr(CO\text{-}880)_{0.4}.TPB_2$	12.0	197–200
		$Ba(CO\text{-}880)_{0.4}.TPB_2$	12.0	215–217
		$Cu(CO\text{-}880)_{[illegible]}.TPB_2$	very unstable	(Ref. 26)
		$Pb(CO\text{-}880)_{0.4}.TPB_2$	12.0	(Ref. 26)
Antarox CO-890	40	$Na(CO\text{-}890)_{0.21}.TPB$	8.4	108–110
		$Mg(CO\text{-}890)_{0.3}.TPB_2$	12.0	60–65
		$Ba(CO\text{-}890)_{0.3}.TPB_2$	12.0	207–220
Antarox CO-850	20	$Na(CO\text{-}850)_{0.42}.TPB$	8.4	55–60 with decomposition
		$Ba(CO\text{-}850)_{0.6}.TPB_2$	12.0	210–215
PEG (1540)	34	$Na(PEG\text{-}1540)_{0.25}.TPB$	8.5	150–155
		$Mg(PEG\text{-}1540)_{0.31}.TPB_2$	10.5	135–138
		$Ba(PEG\text{-}1540)_{0.31}.TPB_2$	10.5	225–230
PPG (1025)	17.36	$Na(PPG\text{-}1025)_{0.49}.TPB$	8.5	–
		$Mg(PPG\text{-}1025)_{0.69}.TPB_2$	12.0	–
		$Ca(PPG\text{-}1025)_{0.69}.TPB_2$	12.0	70–75
		$Sr(PPG\text{-}1025)_{0.69}.TPB_2$	12.0	105–110
		$Ba(PPG\text{-}1025)_{0.69}.TPB_2$	12.0	140–145
PPG (2025)	34.56	$Ca(PPG\text{-}2025)_{0.35}.TPB_2$	12.0	60–65
		$Sr(PPG\text{-}2025)_{0.35}.TPB_2$	12.0	60–65
		$Ba(PPG\text{-}2025)_{0.35}.TPB_2$	12.0	55–60

[a] Poor stability and decomposition where m.p. data are not given [except for $Pb(CO\text{-}880)_{0.4}.TPB_2$ where m.p. was not determined]. All the m.ps. are irreversible with signs of charring at 5° below the minimum of the quoted ranges.

aqueous metal chloride solution (nitrate for lead) (10 cm³ of 0.1M or 1M solution) to an aqueous solution (0.154 g 100 cm⁻³) of the appropriate polyalkoxylate (NP, PEG or PPG). The resulting oxonium ion may be precipitated with excess sodium TPB ($10^{-2}M$), filtered, washed well with water and vacuum dried at 35-50°.

The waxy, thermally unstable magnesium and copper complexes need to be dried over phosphorus pentoxide.

Although the same general method applies to the TPB salts of sodium complexes, concentrated sodium chloride solutions (1M) are needed to coagulate the precipitates prior to final drying over phosphorus pentoxide.

Analytical and spectroscopic characterisation of the white products (pale blue for the copper complex) were in accord[25,26] for the complexes summarised in Table 1. The number of alkoxylate units (AOU) per cation (Table 1) calculated from nmr spectra was deduced from the total number of protons of the alkoxylate chain of each complex molecule as determined from the height of their integrated area in the nmr spectrum in relation to integrations of the TPB protons which were shifted far downfield from those of the alkoxylate protons[25]. Due allowance was made for the phenyl protons associated with the NPs when deducing the number of TPBs associated with each polymer molecule of predetermined molecular mass[25].

The number of alkoxylate units associated with each metal ion obtained from nmr data in the above way was found to be similar to values obtained by chemical analysis. For the NP adducts with bivalent cations, the assessment of 12 alkoxylate units per cation fully supports earlier assessments for calcium, strontium and barium complexes, respectively[9,11,27]. For the PEG complexes, the previously reported ratio of ≈ 10.5 alkoxylate units per bivalent cation[28] has also been found to hold. The alkoxylate:sodium ratios for the complexes in Table 1 are close to the figure of 8 required to wrap the sodium ion completely in order to promote maximum stability[29,30].

Analysis of alkoxylates :

Coordination reactions between alkoxylates and metal cations form the basis of gravimetric, titrimetric and spectrophotometric analytical procedures for alkoxylates[22] (Table 2). Of these, the spectrophotometric methods are the most appropriate to date for analysing alkoxylate non-ionic surfactants in waters and effluents[23]. For the sake of completion, certain other methods for analysing alkoxylates are included in Table 2.

Membrane electrodes with sensors of polyalkoxylate : metal adducts :

Ion-sensing :

Several of the complexes listed in Table 1 form the basis of successful sensors in liquid[9-13] and

TABLE 2—METHODS OF ANALYSING ALKOXYLATES

Method type	Brief description	Reference
Gravimetry	Precipitation of metal ion · alkoxylate complex with	
	potassium hexacyanoferrate(II)	31
	potassium tetraiodobismuthate(III)	32-34
	heteropolyacids	35-39
	sodium tetraphenylborate	40-44
Titrimetry	Metal ion : alkoxylate complex titrated with sodium tetraphenylborate using various methods of end-point detection, including visual indicator (Congo Red)[16,17], potentiometry (with silver indicator electrode[28]), indirect coulometry with biamperometric detection[46] and thermometric titration[47]	27, 28 45-47
Spectrophotometry	Solvent extraction of complexes of polyalkoxylates with metal ions using large polarisable ions like	
	tetrathioisocyanatocobaltate(II) at 620 nm	48-53
	heteropolyacid (molybdenum complex at $\approx$ 650 nm)	54
	picrate (at 378 nm)	15, 55-58
Chromatography (GLC and TLC)	GLC may be used for lower polyalkoxylates by direct methods[59,60,67], cleavage methods may also be employed [60,61] TLC may be used for higher, slightly volatile, oligomers[60,63-66].	59-67
Spectroscopy	UV [60,68] and ir[60 69,70], X-ray fluorescence[69 70]	15, 68-70
Indirect spectrophotometry	Solvent extraction into 1,2-dichlorobenzene of neutral adduct of non-ionic surfactant with potassium tetrathiocyanatozincate(II) Zinc(II) in the extract determined spectrophotometrically after adding 1-(2-pyridylazo)-2-naphthol and triethanolamine	71

PVC matrix membrane[13-18,24] ion-selective electrodes. A successful barium ion-selective electrode system[13,14] is based on the complex of a nonylphenoxypolyethoxylate containing 12 ethoxylate units and 2 mol of tetraphenylborate ion per mole of barium ions [Ba(Antarox CO-880)$_{0.4}$.TPB$_2$] For use in PVC matrix membrane electrodes, this requires a more viscous solvent mediator than the 4-nitroethylbenzene used in liquid membrane electrodes[13]. Both 2-nitrophenyl phenyl ether and 2-nitrophenyl octyl ether satisfy this condition, but the former gives electrodes of superior lifetimes (about 30 days)

PVC matrix membrane electrodes[13] based on [Ba(Antarox CO-880)$_{0.4}$.TPB$_2$] sensor and 2-nitrophenyl phenyl ether solvent mediator have effective linear calibration ranges of 10^{-1} to $\approx 10^{-5} M$ barium ions, near-Nernstian slopes of 28 to 29 mV decade^{-1}, response times of less than 1 min in normal ranges and $\approx$ 5 min near the detection limit, daily drifts of only 1 to 2 mV and long effective *p*H ranges (1.5 to 10). Selectivity coefficients, $k^{pot}_{Ba,B}$, for barium over a large range of ions, B, (interferent, $[B]=10^{-1}M$) are less than 1.8×10^{-2} for B=Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ni, or Cu

Among the possible applications of these PVC matrix membrane electrodes is the potentiometric titration of sulphate with barium ions. Such titrations of 10^{-1} and $10^{-2}M$ solutions of sodium sulphate and sulphuric acid with barium chloride and using the electrode with a calomel reference electrode[13] gave a coefficient of variation corresponding to the theoretical end-point of 0.1%. The break in emf at the end-point for the titration of 1.56 mg of sulphur from sulphate in 15 cm^3 solution exceeds 50 mV. Titrations of the sulphate following oxygen flask combustions of dibenzyl sulphide, S-benzylthiouronium chloride, dibenzyl sulphide+aniline phosphate (5+3) and triphenylphosphonic sulphide gave average sulphur recoveries of 100.25 per cent, thus confirming the technique as a possible application for the barium ion-selective electrode[13]

Other potentiometric titration applications of the barium ion-selective electrode are the titration of sulphate in the presence of chromium(VI)[24] and in the determination of sulphate in sea water and certain natural waters with liquid membrane electrode[72]. The electrode has also been tested for determining sulphate by analate subtraction[73].

In titration work, regard must be had to possible interferences by cations and anions. In this respect, cations, for example potassium, which can be sensed by the barium ion-selective electrode, give distorted titration curves, while *p*H values below 1.5 lead to electrode breakdown[13]. Cations, such as calcium, which interact with sulphate give low sulphate recovery, while anions that interact with the barium titrant lead to apparently high sulphate. Treatment of samples with cation-exchange resins in the sodium form can remove cation interferences, while acidification to *p*H 2 with hydrochloric acid prevents interference from anions, such as phosphate, carbonate, hydrogen carbonate and organic anions[13].

Bauman[12] has successfully used a liquid membrane electrode based on the tetraphenylborate of the strontium-NP (30 ethoxylate units) complex for strontium ion determinations, but naturally barium was absent in these samples.

Tetraphenylborates of sodium and alkaline earth metal ion-complexes with a polypropoxylate [PPG(1025)] have been evaluated for ion-selective electrode qualities in conjunction with various solvent mediators[16,17]. From these a creditable PVC matrix-membrane calcium ion-selective electrode evolved. This was functional over a wide *p*H range (4.5 to > 10) and was based on the Ca(PPG-1025)$_{0.69}$.TPB$_2$ of Table 1 as sensor

and dioctylphenyl phosphonate as solvent mediator. Since the sensor starting materials are noted for their properties and as non-ionic surfactants or for altering the humectant properties of simple glycols and glycerine, they are readily available. This and the ease with which they can be complexed with certain cations, calcium in this case, and precipitated as tetraphenylborates render the sensors readily accessible for ion-selective electrode construction[17]. This can be advantageous when the, evidently much better, calcium ion-selective electrodes based on the more difficult to prepare organophosphate and neutral carrier sensor systems[74] are not at hand or if their enhanced selectivity is not required

Alkoxylate sensing :

The barium ion-selective electrodes discussed above may be used in a converse potentiometric approach for sensing alkoxylates in solution[19]. The observed potentiometric response is an increase of up to ≈100 mV in emf of the barium versus a calomel reference electrode according to the amount of added alkoxylate in the $2 \times 10^{-5} M$ to $10^{-3} M$ range. The response is linear with log[alkoxylate], but is characterised[19] by a break in the linearity which is attributed to the critical micelle concentration (CMC).

The alkoxylate potentiometric response has been observed[19] for various members of the Antarox series of NPs, namely, CO-430 (n=4), CO-630 (n=9), CO-730 (n=15), CO-850 (n=20), CO-880 (n=30) and CO-890 (n=40). Other materials for which the response has been observed[19] include Antarox CA-620 and Triton X-100 (both are octylphenoxypolyethoxylates), Tween 80 (a sorbitan-9-octadecanoatepolyethoxylate) and several alkylpolyethoxylates (Dobanol 27-7, Lutensol AO7 and Synperonic 7) It is interesting to observe the good comparison between experimental (by electrode) literature and the calculated CMC for members of the Antarox series of NPs (Table 3).

TABLE 3—CRITICAL MICELLE CONCENTRATIONS OF ANTAROX NPs[19]

Antarox	Critical micelle concentration/$10^{-4} M$: Experimental by electrode	Literature	Calculated[c] $\ln CMC = A\bar{n} + B$
CO-890	4 6 (0.38 sd)	–	4.5
CO-880	2.5 (0 24)	2.5 to 3 0[a] 1 85[b]	2 6
CO-850	1.4 (0 26)	1.35 to 1.75[a] 1.40[b]	1.5
CO-730	1 1 (0 056)	1.0 to 1 30[a] 1.10[b]	1.11
CO-630	0 83 (0.074)	–	0.80
CO-430	0 60 (0.055)	–	0.60

[a] Hsiao, Dunning and Lorenz, *J Phys Chem.*, 1956, **60**, 657

[b] Schick, Atlas and Eirich, *J. Phys Chem*, 1962, **66**, 1326.

[c] Equation obtained from Reference [a] with A = 0.056 and B = 3 87.

Later research has shown that electrodes where the TPB of the barium complex of Antarox CO-880 in the membrane has been replaced by the TPB of the barium complex of Antarox CO-430, are superior in their response to the non-ionic polyalkoxylates mentioned above. This indicates a further possible application for these electrochemical sensors, for polyalkoxylates are widely used as non-ionic surfactants[22,75].

The Antarox CO-430 electrode has been evaluated[20] for determining Dobanol 25-7, Synperonic 7 and Lutensol AO7 in detergent powder solutions of concentration 0.15% m/v (equivalent to ≈ 0.015% m/v or 150 ppm of the non-ionic surfactant) The recommended procedure is based on known (standard) addition[20]. In this test, 25 cm^3 of 0.15% fully-formulated detergent solutions, containing the non-ionic surfactant being determined, were spiked with non-ionic surfactant of known concentration[20]. Data obtained for Antarox CO-430 electrodes, calibrated by adding aliquots of Synperonic 7 solutions (1 0% m/v) to 25 cm^3 of a 0.15% m/v aqueous solution of fully formulated detergent base, are quoted in Table 4

With regard to more general application, there will be many situations when alkoxylates will

TABLE 4—SOME KNOWN ADDITION DATA OF POLYALKOXYLATE TYPE NON-IONIC SURFACTANTS IN SOLUTIONS OF MODEL AND REAL SAMPLES OF DETERGENT POWDERS DETERMINED BY ANTAROX CO-430 ELECTRODE AND USING SYNPERONIC 7 SPIKES (ADAPTED FROM REF 20)

Nature of sample and of polyalkoxylate (all in fully formulated detergent base) in deionised water	Non-ionic surfactant in solution/% m/v: Expected	Found	s.d/10^{-4}	(n)
Synperonic 7 (model power)	0.0150[a]	0 0151	1.2	(5)
Dobanol 25-7 *plus* (model)	0.0150	0 0150	1.7	(5)
Synperonic 7 (1+1) (powder)	0.0150	0.0150	1.7	(5)
Synperonic 7 (model powder)	0.0080	0.0079	0.8	(4)
Synperonic 7 (model powder)	0.0320	0.0321	5.4	(4)
Fully formulated detergent powder 'A' containing Lutensol A07	0.0150	0 0146	2.5	(15)
Fully formulated detergent powder 'B' containing a non-ionic surfactant of unspecified alkyl	0.0150	0.0150	1.4	(12)

[a]: 0.0150% m/v = 150 ppm

be present at considerably lower levels than the examples of Table 4. In this respect, it should be noted that the Antarox CO-430 electrode will respond to less than 0.15 mg dm^{-3} ($10^{-7}M$) of Antarox CO-880 in deionised water[20], but it is a pity that the electrode response times are so long (≈30 min) at such low levels of alkoxylate.

Conclusion :

Complexes between metal ions and polyalkoxylates offer a new interesting area of study in chemistry of such considerable practical application that they also merit study with regard to ion-dipole interactions and structure, by those who are more theoretically oriented. The information so obtained can then be used to plan improved systems that can be applied to obtain better sensors and analytical methods and to enhance the use of these materials as selective extractants for metal ions.

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The Cumulation of Methylmercury and Phenylmercury Species on Alga

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The cumulation of methylmercury and phenylmercury species on the alga *Chlorella kessleri* has been radiometrically investigated as a function of algal cells, the species studied and hydrogen ion concentration, in the absence and presence of different metal salts and complexing agents. It has been found that the cumulation factor F decreases with the increase of methylmercury and phenylmercury concentration and with the increase of *p*H, but is not influenced by the presence of metal salts. Reagents forming negatively charged complexes with methylmercury and phenylmercury cations decrease the F-value. The cumulation of species studied was quantitatively described using the affinity constants.

THE biotransformation of inorganic mercury, methylmercury and phenylmercury chlorides, has been investigated in our previous papers[1,2] using different types of algae. It has been found that all species studied were cumulated very rapidly in the algae. However, from the second day onwards methylmercury and phenylmercury changed into less toxic inorganic mercury. In continuation of these studies, the physico-chemical investigation of the cumulation of methylmercury and phenylmercury species has been carried out to describe quantitatively the cumulation of the above species

Experimental

All reagent used, unless otherwise stated, were of A.R. quality. Hydrochloric acid and sodium hydroxide, (superpure, Merck) were used for adjusting the *p*H.

Solutions for radionuclides (Amersham, England) were prepared by dissolving methylmercury-203 chloride (specific activity 2.5 GBq/g Hg) and phenylmercury-203 acetate (specific activity 2 GBq/g Hg) in 0.01 *M* NaOH.

Algologically and bacteriologically pure strains of the alga *Chlorella kessleri* were used in the experiments. The mean geometric volume of one cell, $V_a = 3.5 \times 10^{-11}$ cm^3 and the mean geometric surface, $S_a = 4.5 \times 10^{-7}$ cm^2 were calculated from measured size of the cells.

Well-type scintillation NaI (Tl) counter was used for the measurements of the radioactivity and Radiometer PHM-52 (Copenhagen, Denmark) for the determination of equilibrium *p*H values.

The cumulation of methylmercury and phenylmercury species was investigated in the manner described earlier[3,4]. An appropriate volume of alga suspension (containing a known amount of algal cells) was centrifuged and transferred into test tubes containing methylmercury or phenylmercury species (labelled with mercury-203), HCl (or NaOH), different metal salts or reagents of known concentration (total volume 10 ml) and the mixture shaken for 1 hr. The equilibrium *p*H value, the radioactivity of algae (A_a) and that of the medium (A_m) were measured and the cumulation factor F (the ratio of the concentration of the species studied in alga and in aqueous phase) was calculated according to eq. (1)

$$F = \frac{A_a}{A_m N_a V_a} = \frac{D}{N_a \bar{V}_a} \qquad \ldots (1)$$

where N_a is the number of algal cells per cm^3, V_a is the mean geometric volume of one cell in cm^3, D is the distribution ratio of the species studied. All experiments were carried out at 22 ± 1°.

Results and Discussion

The influence of *p*H on the cumulation of methylmercury and phenylmercury species is illustrated in Fig 1. At *p*H <7, the cumulation practically does not depend on *p*H; in these conditions methylmercury and phenylmercury are present predominantely as CH_3HgCl and C_6H_5HgCl complexes. The decrease of the F-value at higher *p*H is probably connected with the formation of more soluble CH_3HgOH and C_6H_5HgOH complexes. This assumption was confirmed by the fact that the addition of NaCl into alkaline medium leads to the increase of F-value The kinetics of the uptake is rather rapid; the equilibrium was reached in less than 1 hr shaking.

It has been found that the F-values (in otherwise constant conditions) does not depend on the concentration of algal cells ($N_a = 7.5 \times 10^6 - 6 \times 10^8$ cells.cm^{-3}). This allows the adjustment of the N_a value in such a manner that the measurement of distribution ratio is very precise.

The highest values of cumulation factor (F_0) or distribution ratio (D_0) were found at lowest concentrations of the species studied and at highest algal cells concentration. The increase of methylmercury
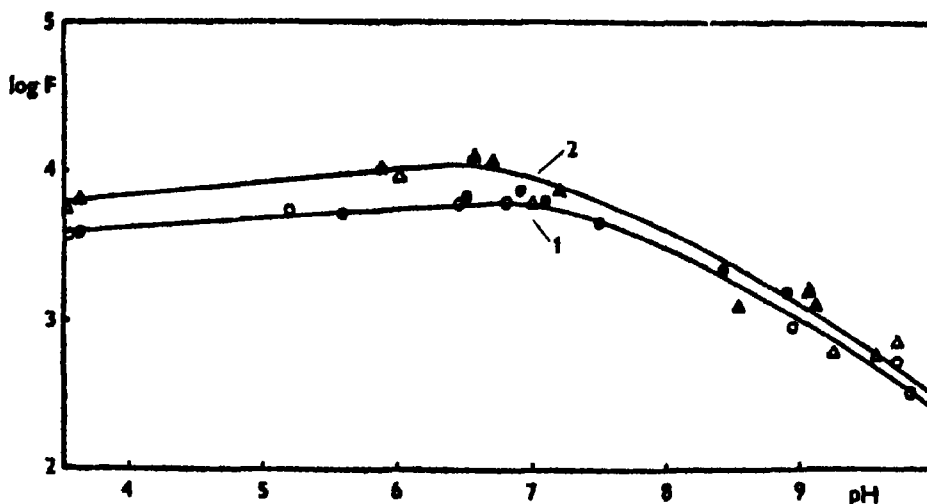
Fig 1. The dependence of the cumulation factor F of methylmercury (curve 1) and phenylmercury species (curve 2) on pH (total concentration 3×10^{-6} mol. dm^{-3}, $N_a = (3\text{-}5) \times 10^{6}$ cells. cm^{-3}, free points—1 hour shaking, full points—3 hours shaking).

and phenylmercury concentration leads to a decrease of the cumulation (F or D-values) because of the limited capacity of the algal cells to cumulate the species studied. Similar results were obtained in the study of the cumulation of alkali metals and alkali earths on alga[4].

The cumulation of methylmercury chloride or phenylmercury chloride (RHgCl) on alga can be quantitatively described using the affinity constant K_M[4]

$$K_M = \frac{[RHgClA]}{[RHgCl]\,[A]} \quad (2)$$

where [RHgClA] and [RHgCl] denote the equilibrium concentration of the species studied in alga and in aqueous phase, respectively, [A] denotes the "free capacity" of algal cells to cumulate RHgCl.

The K_M value can be calculated from the following equations[4]

$$\frac{F_0}{F} - 1 = K_M\,[RHgCl] \quad (3)$$

or at constant N_a and V_a

$$\frac{D_0}{D} - 1 = K_M\,[RHgCl] \quad (4)$$

The experimentally determined ratio D_0/D at different equilibrium concentration of RHgCl (determined from the radioactivity in the aqueous phase) was used for the calculation of K_M values (Table 1).

It has been found that the F-value of methylmercury chloride (pH ~5.2 in the presence of 0.004 M NaCl) also decreases in the presence of an excess of phenylmercury chloride. Similarly, the F value of phenylmercury chloride decreases in the presence of methylmercury chloride. On the other hand, F value of both the species is not influenced in the presence of 0.005 M $Mg(NO_3)_2$, $Sr(NO_3)_2$, $ZnSO_4$, $CdSO_4$ or 0.001M $CuSO_4$, $Cr(NO_3)_3$. It follows from these results that the mechanism of the

TABLE 1—AFFINITY CONSTANT K_M OF METHYLMERCURY AND PHENYLMERCURY CHLORIDES IN 0.004 M NaCl (pH ~ 5.2)

Species	$\frac{D_0}{D}$	$-\log$ [RHgCl]	$\log K_M$
CH_3HgCl	2 6	5.65	5.85
	4.6	5.40	5.96
	5.5	5.23	5.88
	14	4.85	5.96
	21	4.62	5.92
	50	4.50	6.19
		mean	5 96±0.12
C_6H_5HgCl	3.5	5.85	6.25
	4	5.55	6.03
	6	5.50	6.20
	9	5 00	5.90
	24	4.96	6.32
	40	4.69	6.28
		mean	6 16±0.16

cumulation of CH_3HgCl and C_6H_5HgCl is quite different from that of metal ions

The stability constant of methylmercury chloride ($\log \beta_1 = 5.5$)[5] and phenylmercury chloride ($\log \beta_1 = 5.8$)[5] is rather high and because of this the cumulation of these species can be decreased only in the presence of reagents forming very stable negatively charged complexes with CH_3Hg^+ or $C_6H_5Hg^+$ cations such as sodium thiosulphate ($\log \beta_1 = 10.9$)[6].

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Separation of Nickel by Solvent Extraction and Cation-Exchange. Determination of Nickel in Mineral Waters

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A method for the isolation of nickel from mineral waters by solvent extraction and cation exchange is described. The nickel is first preconcentrated from the waters by chloroform extraction in its dimethylglyoximate form at *p*H 7.4-7.6. The chloroform extract is then mixed with THF and methanol containing hydrochloric acid, and passed through a column of Dowex 50-X8 (H^+ form). After removal of dimethylglyoxime, chloroform and THF by washing the resin with methanol-HCl, nickel is eluted with 6*M* HCl and determined by a.a.s. with an air-acetylene flame The method was successfully applied to determine nickel in bottled mineral waters in which nickel in the range from 0.3 to 30 μg Ni/litre was found.

THE determination of trace quantities of nickel in natural waters and waste waters is gaining increasing importance with the growing interest in pollution of the environment with this and other heavy metals.

Preconcentration of nickel, mainly together with several other metal pollutants, is carried out before its quantitative determination. For isolation of trace amounts of nickel from natural and waste waters the best separation methods are based on liquid-liquid extraction of nickel with dithiocarbamates or as other nickel complexes[1-10].

In the present paper, a combination of separation techniques is described, which utilizes chloroform extraction of nickel dimethylglyoximate as the first preconcentration step followed by cation-exchange enrichment of nickel directly from the organic extract.

Experimental

Apparatus and reagents :

The strongly acidic cation exchanger Dowex 50-X8 (Bio-Rad AG 50W-X8, 100-200 mesh ; H^+ form) was used. A slurry of the resin (4 g) was prepared with a few ml of 6 *M* HCl and poured into the ion-exchanger column using 50 ml of the same acid as a rinse and to purify the exchanger. Subsequently, the resin was washed with tetrahydrofuran (THF) prior to pretreatment of samples.

Standard solutions of Ni(II) in 6 *M* HCl was prepared from a stock solution containing 1 mg Ni(II) per ml of 6*M* HCl. MeOH-HCl mixture with 1 *M* overall acidity was prepared by diluting 85 ml conc. HCl to 1 litre with methanol. 10 ml of this diluted to 100 ml with methanol gave the MeOH-HCl mixture of 0.1*M* overall acidity, which is used for the ion-exchange separation of nickel. $CHCl_3$-THF-MeOH solution of 0.1 *M* overall acidity was prepared by mixing 30 ml of $CHCl_3$ with 60 ml of THF and 10 ml of MeOH-HCl mixture of 1 *M* overall acidity. Other reagents used were 10% aqueous solution of hydroxylamine hydrochloride, aqueous ammonia (1 : 1) and a 10% solution of dimethylglyoxime in ethanol.

For the determination of nickel, a Perkin-Elmer Atomic absorption Spectrometer Model 303 was used with the following instrumental settings : uv grating ; wavelength 232.5 nm ; scale expansion up to 2X ; slit width 3 (0 3-0.2 nm bandpass) ; nickel hollow-cathode lamp at 25-40 mA ; standard burner head ; acetylene pressure 8 psig (7.0 on flow meter scale) ; air pressure 30 psig (9.0 on flow meter scale) ; noice suppression up to 2.

When the measurements were done with 6 *M* hydrochloric acid solutions, a sensitivity (1% absorption) of 0.24 ppm of nickel was obtained.

The ion-exchange columns used for the separation of nickel from the organic extracts were of the type and dimensions described earlier[11].

Determination of distribution coefficients : The distribution coefficients (K_d-values) of nickel in the various media employed for the cation exchange separations were determined by using the batch method[12].

Procedure :

To 0.5-1.0 litre of the water sample are added 10 ml of conc. HCl and 5 ml of the hydroxylamine hydrochloride solution. The *p*H of the mixture is adjusted to 7.4 to 7.6 by the addition of dilute ammonia solution (1 : 1) and it is transferred to a 2 litre separatory funnel using a few ml of water as a rinse. 5 ml of the dimethylglyoxime solution is added to the sample mixture and shaken for 1 min. The nickel dimethylglyoximate is extracted with 20 ml of chloroform using a shaking time of 5 min.

The extraction is repeated with two 20 ml portions of chloroform, shaking 2 min each time. The three extracts are combined.

To the combined chloroform extracts (about 60 ml) is added 20 ml of the MeOH-HCl mixture (overall acidity 1 *M*) and diluted with 120 ml of THF. The resulting solution (the sorption solution, overall acidity 0.1 *M*) is passed through a 4 g column of the cation exchanger (pretreated with 20 ml of the $CHCl_3$-THF-MeOH solution) at a flow rate of about 1.7 ml/min. The resin bed is washed with 5 ml $CHCl_3$-THF-MeOH solution, 10 ml of MeOH-HCl mixture (overall acidity 0.1 *M*) and 5 ml 0 1 *M* hydrochloric acid in this order. The nickel is then eluted with 100 ml of 6 *M* HCl.

The eluate is evaporated to dryness on a steam-bath and the residue is dissolved in 10 ml of 6 *M* hydrochloric acid. This solution is aspirated into the air-acetylene flame. Calibration curves are constructed by aspirating suitable standard solutions of nickel before and after each batch of samples.

Results and Discussion

Separation of nickel :

Atomic-absorption measurements of the nickel in the chloroform extracts did not give either the required sensitivity or reproducible results. The nickel was therefore stripped from the organic phase using dilute HCl and the assay was completed after wet-ashing of the co-extracted organic compounds. However, this very tedious procedure was abandoned in favour of the ion-exchange technique described in the procedure which in combination with the extraction step gave results of high accuracy and reproducibility. It is seen from Table 1 that this procedure allows the quantitative isolation of both μg and mg amounts of nickel.

TABLE 1—EFFECT OF CONCENTRATION ON NICKEL RECOVERY FROM TAP WATER

Amount of nickel added to 1 litre of water sample, μg	Nickel found μg/litre	%
12	11.8	98.5
100	103	103
500	512	102 5
1000	998	99.8

By means of the ion-exchange procedure the nickel is separated from the chelating agent dimethylglyoxime and chloroform without the need of evaporation or back-extraction and wet-ashing. The presence of tetrahydrofuran is necessary in the $CHCl_3$-THF-MeOH solution to obtain a homogeneous solution, and methanol is the component regulating the flow rate through the ion-exchange column. In absence of methanol, the viscosity of the sorption solution is extremely low and a very high flow rate is attained at which complete adsorption of nickel is not assured. Hydrochloric acid has to be present in the mixture so that the nickel remains in the ionic form which is adsorbed on the cation-exchanger during the sorption process. After adsorption, the residual chloroform, tetrahydrofuran and dimethylglyoxime are removed by washing the resin bed with the MeOH-HCl mixture.

The measurement of the batch distribution coefficients of nickel in all the media employed for the cation-exchange separation of this element gave the results for K_d as 1940 in $CHCl_3$-THF-MeOH medium, 4380 in MeOH-HCl mixture, and 977 and < 1 in 0.1 and 6 *M* HCl, respectively.

Nickel is thus found to be very strongly retained by the resin from the organic as well as aqueous 0.1 *M* hydrochloric acid solutions so that this method is suitable for the quantitative separation of both μg and mg amounts of this element.

TABLE 2—DETERMINATIONS OF NICKEL IN SAMPLES OF BOTTLED MINERAL WATER

Trade name	Nickel content μg/litre A	B
Bonaqua	0 25	0 26
Petersquelle	0.34	0.34
Ausseer Heilquelle	0 53	0 54
Römerquelle	1.30	1.33
Sixtina	2 89	2 99
Donat	3 49	3.51
Severinquelle	3 87	3 63
Güssinger	4 84	4 82
Vitusbrunnen	5 24	5 15
Radenska	5 22	5 38
Preblauer (Ebriachquelle)	29.9	29.8

*A—Nickel contents determined by a.a.s following solvent extraction and cation-exchange of nickel

B—Same as for A, but after deduction of 2.0 μg Ni added to the sample before application of the procedure.

Application to natural waters :

Table 2 gives the results obtained when this procedure was applied to the analysis of 11 mineral water samples.

Comparison of the results listed in columns A and B of Table 2 shows that the amounts of nickel added were recovered quantitatively in all cases, i.e. nickel is not lost during the separation procedures.

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Extraction of Zinc(II) as Chloride by High Molecular Weight Amine, Amberlite LA-1

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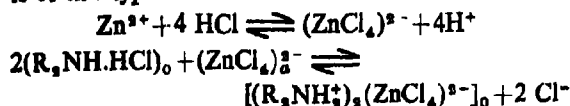
A rapid and selective method for the extraction of milligram amounts of Zn(II) from hydrochloric acid solution with liquid anion exchanger, Amberlite LA-1, in nitrobenzene has been proposed. Quantitative extraction has been achieved in the hydrochloric acid conc range 2-4 *M*. Diluents having high dielectric constant values show improved extraction results, compared to benzene, xylene, toluene, chloroform and carbon tetrachloride. The effect of such variables as hydrochloric acid conc., contact time, stripping time and extractant conc was studied and the effect of foreign ions investigated. The separation of zinc from several synthetic mixtures is also found quantitative. The probable composition of the extracted species has been deduced from the extraction data.

IN recent years, solvent exraction with high molecular weight amines and quaternary ammonium compounds has been extensively used as a promising technique in industries and atomic energy programmes. The applications include the removal of toxic elements such as Hg, As, Cd, Zn, Cu, Pb, Cr etc. for pollution abatement from industrial effluents and recovery of fertile and fissionable materials from irradiated fuel elements at atomic energy centres.

The amines, due to their unique anion exchange ability, extract anionic metal complexes from the aqueous phase. Separation and estimation of such type of metals through liquid cation exchangers have been carried out in this laboratory[1-5]. The liquid anion exchanger, on the other hand, is the point of interest to explore in the extraction of toxic metals. The present work reports on the selectivity of Amberlite LA-1 for the extraction of zinc(II) chlorocomplex. No such work is reported in the literature[6-9].

The mechanism of extraction of zinc from aqueous hydrochloric acid solution with the secondary amine, pretreated with hydrochloric acid, is of this type :

$$Zn^{2+} + 4\,HCl \rightleftharpoons (ZnCl_4)^{2-} + 4H^+$$

$$2(R_2NH.HCl)_o + (ZnCl_4)^{2-}_a \rightleftharpoons [(R_2NH_2^+)_2(ZnCl_4)^{2-}]_o + 2\,Cl^-$$

where o = organic phase and a = aqueous phase.

The secondary amine and its salt with anionic chlorocomplex of zinc are essentially insoluble in aqueous solutions but exhibit high solubility in organic solvents.

Experimental

Apparatus : A single pan balance, SICO Popular Model, Scientific Instrument Co., Calcutta was used for taking weights. Separatory funnels (150 ml) were used for extraction experiments.

Reagents :

The liquid anion exchanger, Amberlite LA-1, manufactured by the Rohm and Haas Co., Philadelphia, USA, and supplied by B.D.H., Poole. England was used without further purification. Nitrobenzene (Sarabhai M. Chemicals, GR) was used as diluent. The amine was suitably diluted with nitrobenzene and converted to its chloride form by equilibrating with hydrochloric acid for 5 min The molar concentration of the amine was determined by stripping the chloride by sodium hydroxide solution and then titrating the chloride with standard silver nitrate solution using potassium chromate as indicator[9,10].

$ZnSO_4.7H_2O$ (B.D.H., A.R.) was used for analysis. A stock solution of zinc (6.5 mg/ml) was prepared in double deionised water and the solution standardized by complexometric titration with EDTA (disodium salt) using xylenol orange as an indicator[11].

The chemicals and solvents used were all of analytical grade unless otherwise mentioned.

General extraction procedure :

The procedure was based on solvent extraction technique. The ratio of the volumes of aqueous phase and the organic phase was maintained at 1 : 1. In a separatory funnel, the aqueous phase was made up from a portion of the solution containing 6.5 mg of zinc. Standard hydrochloric acid was added to maintain the required acid strength. The total volume of the aqueous phase was made up to 10 ml. The aqueous phase was equilibrated with 10 ml of 5% v/v Amberlite in nitrobenzene (amine : nitrobenzene = 1 : 20 by volume) for 5 min. The equilibration time was varied from 1-10 min and it was found that the distribution coefficient reached a constant value within 2 min. However, the equilibration time was fixed at 5 min. All the experiments were carried out at 27±1°. The two layers were

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allowed to settle for 10-15 min. The organic phase was then separated carefully to another separatory funnel. The aqueous phase was collected, the excess acid was neutralised by ammonia solution and the amount of zinc present in the aqueous phase was determined by EDTA titration. Then, 10 ml of 2*M* nitric acid solution was added to the organic phase and the mixture was shaken for 5 min. The two phases were allowed to settle, the organic phase was separated carefully and the corresponding aqueous phase (acid extract) was collected and neutralised by ammonia solution. The amount of zinc extracted in that phase was determined

Results and Discussion

Hydrochloric acid concentration :

The extraction behaviour of zinc(II) with Amberlite LA-1 at various acid concentrations is given in Fig. 1. The experiments were performed with constant extractant concentration (5% v/v) and constant

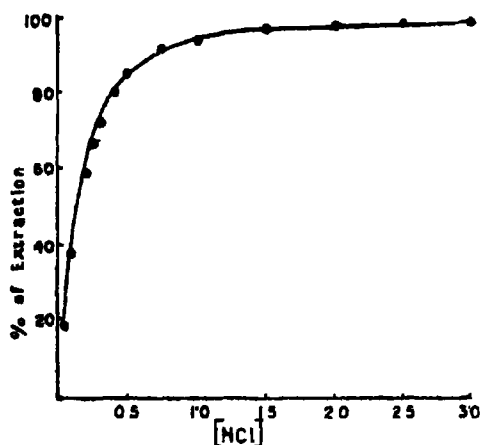



Fig. 1. Extraction of Zn(II) with Amberlite LA-1 as a function of [HCl] in molarity

metal concentration ($9.9\times10^{-3}M$). The extraction of zinc increases with increased hydrochloric acid concentration and becomes quantitative at 2*M* and onwards. The optimum hydrochloric acid range for quantitative extraction is therefore from 2*M* onwards. The distribution ratio was calculated from the extraction data using the relation

$$D=\frac{V}{V'}\left(\frac{100}{100-x}-1\right)$$

where V and V' are the respective volumes of the aqueous and organic phases, respectively and x is the percentage of zinc extracted[13].

In order to evaluate the probable reaction mechanism of Zn(II) with chloride ion, the extraction, at constant ionic strength (2.3*M*), was carried out with varying amount of hydrochloric acid Sodium sulphate was used to maintain the constant ionic strength. Plot of log D against log [Cl] produces a straight line (Fig. 2) with a slope of 2.1 indicating the formation of $(ZnCl_4)^{2-}$ in the aqueous phase. At lower chloride concentration the formation of $(ZnCl_3)^-$ is also expected. Therefore, the reaction in the aqueous phase is proposed to be :

$$Zn^{2+}+3\,HCl \rightleftharpoons (ZnCl_3)^-+3H^+$$

$$Zn^{2+}+4\,HCl \rightleftharpoons (ZnCl_4)^{2-}+4H^+$$

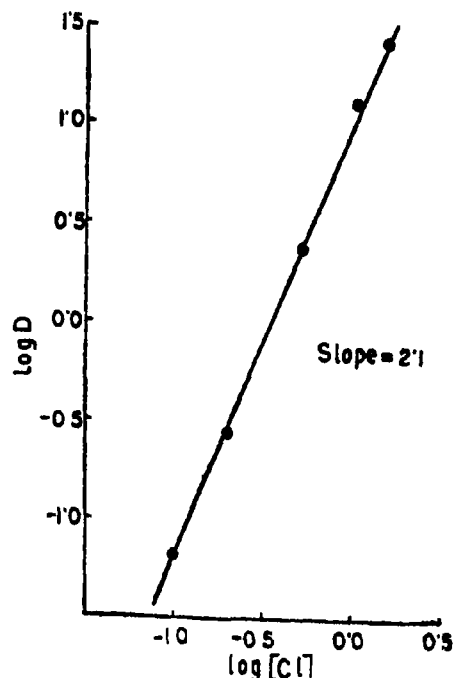



Fig. 2. Plot of log D against log [Cl] at constant [amine].

Amberlite LA-1 concentration :

At constant concentration of zinc ($9.9\times10^{-3}M$) and hydrochloric acid (2*M*), the extraction of zinc as a function of Amberlite LA-1 concentration in nitrobenzene was carried out. The extraction of zinc is quantitative provided the secondary amine : zinc molar ratio is ≥2. Plot of log D against log [Amberlite LA-1] produces a straight line (Fig. 3) with slope 2. Hence the extraction mechanism of

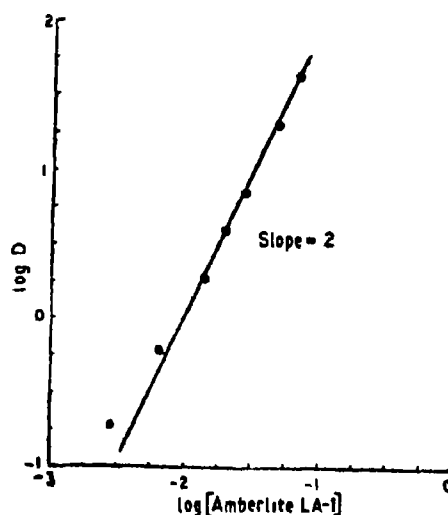
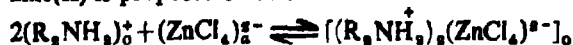



Fig 3. Plot of log D against log [Amberlite LA-1] at 2*M* HCl.

zinc(II) is proposed to be :

$$2(R_3NH_3)^+_o + (ZnCl_4)^{2-}_a \rightleftharpoons [(R_3\overset{+}{N}H_3)_2(ZnCl_4)^{2-}]_o$$

The zinc(II) : Amberlite LA-1 ratio in the extracted species is therefore 1 : 2.

Diluents :

Zinc was extracted with 5% Amberlite LA-1 solution in various diluents (Table 1). The results indicate quantitative extraction of zinc with nitrobenzene which has a high dielectric constant. But the extraction of zinc in benzene (a diluent of low dielectric constant) is more than that in other diluents of high dielectric constant. Hence a clear conclusion cannot be drawn for the diluents used for extraction. The dielectric constant is not the only factor involved.

TABLE 1—EFFECT OF DILUENTS ON EXTRACTION OF ZINC

Diluents	Dielectric constant	Metal extracted (%)	Distribution ratio (D_{Zn})
n-Hexane	1.9	66.5	2 0
Carbon tetrachloride	2.2	30.6	0 4
Benzene	2.3	79.8	3 9
Xylene	2 4	75.7	3 1
Toluene	2 4	53.2	1.1
Chloroform	4 8	15 7	0 1
Butanol	16.1	59 0	1 4
Nitrobenzene	35 7	97 7	41 7

Equilibration time and stripping time :

The contact time was varied from 1 to 10 min. The distribution ratio reached a constant value after 2 min of shaking and back extraction was complete within 5 min. Therefore, the optimum equilibration period was chosen as 5 min in all the experiments.

Metal ion concentration :

Loading experiments, at constant concentration of both amine and hydrochloric acid, were carried out by varying amounts of zinc. More than 96.5% of zinc was extracted from 0.065 to 1.30 g/l under optimum extraction conditions. Fig. 4 shows plot of log $[Zn^{2+}]_o$ against log $[Zn^{2+}]_a$. The ratio of metal to amine concentration in organic phase is found to be 1 : 2 which again supports the proposed extracted species as $[(R_3NH_3^+)_2(ZnCl_4)^{2-}]$.

Extractive separations :

The effect of diverse ions on the quantitative extraction of Zn(II) at optimum condition is shown in Table 2. The metal ions like mercury, cadmium, lead, iron, bismuth and copper are coextracted. The tolerance limits for such ions as cobalt, aluminium, chromium, fluoride and iodide are low (shown in Table 2). Above these limits extraction decreases. Calcium, strontium, barium, magnesium, manganese, nickel, sulphate, phosphate and bromide do not interfere with the extraction of zinc.

TABLE 2—EFFECT OF DIVERSE IONS ON THE EXTRACTION OF Zn(II) WITH AMBERLITE LA-1

[Zinc(II) 6.5 mg ; [HCl] 2 *M*]

Diverse ions	Amount added	Source	Zinc extracted (%)
Ca^{2+}	350 mg	$CaCl_2.2H_2O$	97.4
*Sr^{2+}	350 mg	$SrCl_2.6H_2O$	97.4
*Ba^{2+}	350 mg	$BaCl_2.2H_2O$	97.4
Mg^{2+}	200 mg	$MgSO_4.7H_2O$	97.4
Mn^{2+}	150 mg	$MnCl_2.4H_2O$	97.6
Ni^{2+}	120 mg	$NiSO_4.7H_2O$	97.4
Co^{2+}	15 mg	$CoSO_4.6H_2O$	96 5
Al^{3+}	5 mg	$Al(NO_3)_3.9H_2O$	96.5
Cr^{3+}	2 mg	$Cr_2(SO_4)_3.6H_2O$	96.0
SO_4^{2-}	800 mg	$MgSO_4.7H_2O$	97 4
PO_4^{3-}	450 mg	Na_2HPO_4	97.4
Br^-	250 mg	KBr	96 5
F^-	40 mg	NH_4HF_2	96.5
I^-	20 mg	KI	96.0

* $Zn(OAC)_2$ was used instead of $ZnSO_4$.

Separation of zinc from synthetic mixtures :

Quantitative separation of zinc from some synthetic mixtures was attempted and the results are shown in Table 3. Figures in parenthesis against an ion indicate the amount of the ion present in milligrams.

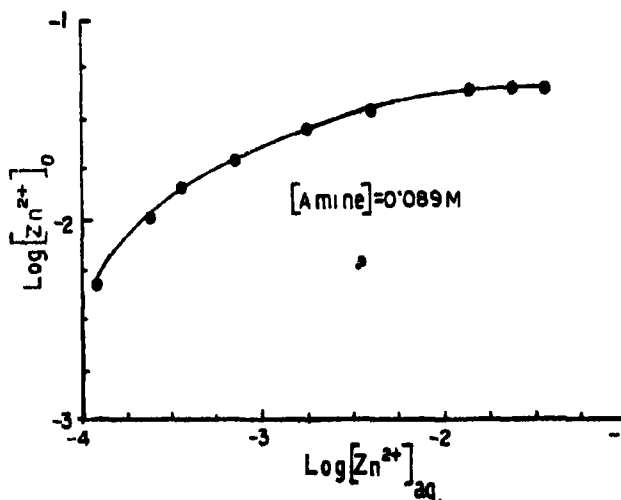



Fig. 4. Plot of log $[Zn^{2+}]_o$ vs log $[Zn^{2+}]_a$.

TABLE 3—QUANTITATIVE SEPARATION OF ZINC(II) FROM SYNTHETIC MIXTURES USING AMBERLITE LA-1

[Zinc(II) 6.5 mg ; [HCl] 2*M*]

Sample No.	Mixture taken (mg)	Zinc extracted (%)
*1.	Ca^{2+}(175)+Sr^{2+}(175)	96.5
*2.	Ca^{2+}(175)+Ba^{2+}(175)	98.6
3.	Ca^{2+}(175)+Mg^{2+}(100)	96.5
*4.	Ba^{2+}(175)+Sr^{2+}(150)	98.0
5.	Mn^{2+}(50)+Ni^{2+}(50)	97.4
6.	Mn^{2+}(60)+Co^{2+}(8)	96.5
7.	Mn^{2+}(60)+Al^{3+}(2)	97.4
8.	Ni^{2+}(50)+Co^{2+}(8)	97.4
*9.	Ca^{2+}(100)+Sr^{2+}(100)+Ba^{2+}(100)	97.4
10.	Mn^{2+}(20)+Ni^{2+}(20)+Co^{2+}(5)	96.5
11.	Mn^{2+}(15)+Ni^{2+}(15)+Al^{3+}(2)	96 0
12.	Ni^{2+}(10)+Co^{2+}(5)+Al^{3+}(2)	96.0

* $Zn(OAC)_2$ was used instead of $ZnSO_4$.

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Solvent Extraction Studies on Thiocyanate Complexes of Zinc(II), Cadmium(II) and Mercury(II)

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The extraction behaviour of zinc(II), cadmium(II) and mercury(II) thiocyanate complexes has been studied in some oxygenated solvents, high molecular weight amines, tributyl phosphate and pyridine. The effect of different variables on extraction has been investigated The extracting species have been identified using loading ratio data and by the method of slope analysis. On the basis of extraction data some mutual separations and separations from other commonly associated elements have been carried out. Relative merits and limitations of different extraction systems are discussed

THE thiocyanate ion is a well known ligand and forms complexes with numerous metal ions which are usually stoichiometrically analogous to the corresponding halo complexes. In view of its strong complexing nature this ion has been widely employed in various areas of chemical analysis including solvent extraction of metal ions[1]. Earlier reports indicate that a large number of investigations have been carried out on the extraction of metal thiocyanate complexes in different extraction systems. However, not much work[1,2] was reported on the extraction of zinc(II), cadmium(II) and mercury(II) as thiocyanates. The separations involving cadmium and mercury are of particular interest to environmentalists as the two elements are serious pollutants of the biosphere

Studies were initiated in this laboratory sometimes back on the extraction of Zn(II), Cd(II) and Hg(II) thiocyanate complexes in some oxygenated solvents[3], high molecular weight amines (HMWA)[4-7] and in non-polar solvents in the presence of neutral donors like tri-*n*-butyl phosphate[8] and pyridine[9]. These investigations mainly dealt with the studies on the mechanism of extraction and utilized the extraction data for obtaining some typical separations of metal ions.

The present paper summarizes the results of these investigations on the extraction of thiocyanate complexes of Zn(II), Cd(II) and Hg(II). The extracting species have been mainly identified by the method of slope analysis However, in the case of extractions in high molecular weight amines, the extracting species have also been identified by extraction isotherms and analysis of the organic extract at the maximum loading conditions. In Hg(II)-thiocyanate neutral ligand systems, the species could not be identified because of nonconclusive results. The extraction behaviour of some other commonly associated elements has also been studied under identical conditions and based on the extraction data some mutual binary separations have been proposed. Attempts have been made to compare the efficiency of different systems for attaining metal ion separations involving Zn(II), Cd(II) and Hg(II).

Experimental

All inorganic chemicals and organic solvents used were of analytical grade. Primene JM-T and Amberlite LA-1 (Rohm and Haas Co., U.S.A.) and Alamine 336 and Aliquat 336 (General Mills, Inc., U.S.A.) were all practical grade materials and used without further purification. The metal ion solutions were generally prepared from sulphate salts and standardised by standard methods. ^{54}Mn, ^{60}Co, ^{65}Zn, ^{110m}Ag, ^{114m}In, ^{115m}Cd, ^{203}Hg and ^{204}Tl radioisotopes, procured from the Bhabha Atomic Research Centre, Bombay, were used as tracers for the distribution studies. The distribution ratio and percent extraction were determined by the usual method.

Results and Discussion

Extraction in oxygenated solvents :

The extraction behaviour of zinc(II), cadmium(II) and mercury(II) was studied from aqueous thiocyanate solutions into *n*-butanol, nitrobenzene and ethyl acetate (Fig. 1). Generally, the extractions are poor in nitrobenzene. The extraction of zinc(II) increases upto a thiocyanate concentration of 0 1M and thereafter becomes almost constant On the other hand the extraction of mercury(II) decreases upto 0.1M and remains almost constant thereafter Cadmium(II), thallium(I) and thallium(III) show negligible extraction in all the solvents.

Mercury(II) can be separated from cadmium(II), thallium(I) and thallium(III) by extracting it into *n*-butanol from $\leqslant$ 0.02M thiocyanate solution Zinc(II) can be separated from cadmium(II), thallium(I) and thallium(III) by extracting into *n*-butanol or ethyl acetate at thiocyanate concentration $\geqslant$0.1M.

Extraction of thiocyanate complexes of zinc(II), cadmium(II) and mercury(II) in HMWA :

The extraction behaviour of Zn(II), Cd(II) and Hg(II) from aqueous thiocyanate solutions, as studied in chloroform and benzene solutions of
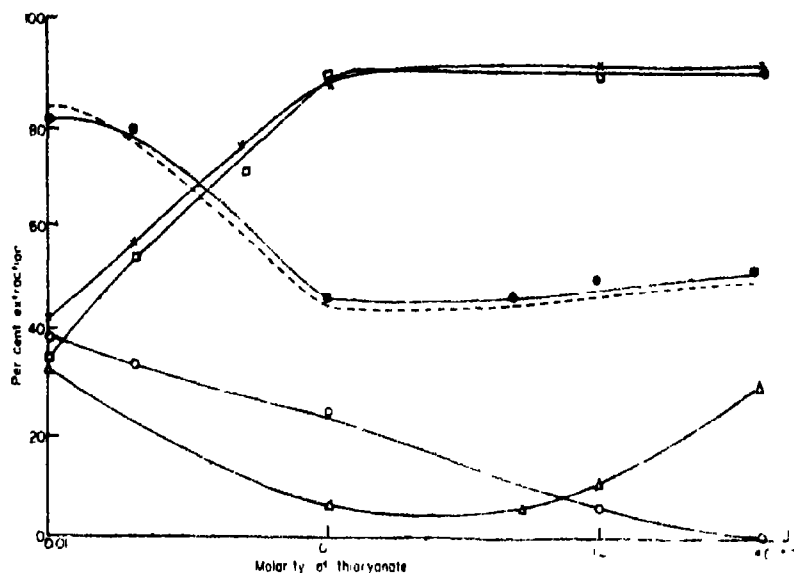
Fig 1. Extraction of Zn(II) and Hg(II) from thiocyanate solutions by oxygenated solvents Zn(II) ×-*n*-butanol, □-ethyl acetate Hg(II) : ●-*n*-butanol (equilibrated), - - - -*n*-butanol (unequilibrated), ○-nitrobenzene, △-ethylacetate.
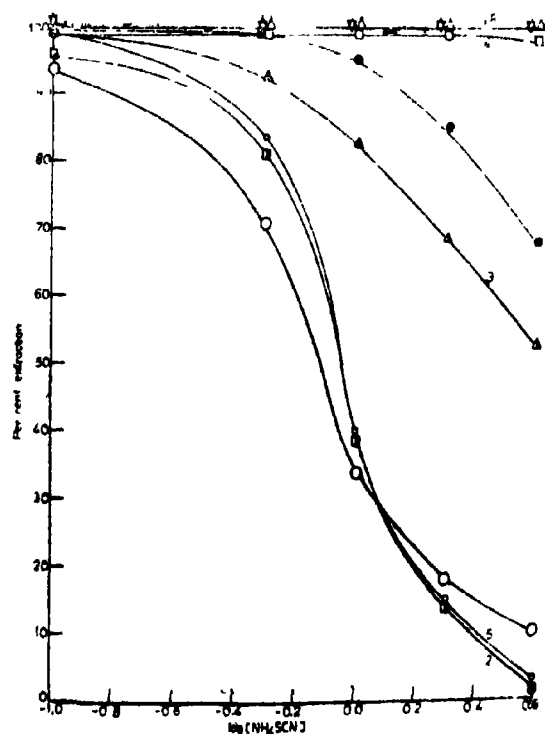
Fig. 2. Extraction of Zn(II) from NH_4SCN solutions by various 0.1*M* amines in chloroform and benzene. Chloroform solvent : (1) Primene JM-T ; (2) Amberlite LA-1 ; (3) Alamine 336 ; (4) Aliquat 336. Benzene solvent : (5) Primene JM-T , (6) Amberlite LA-1 ; (7) Alamine 336 ; (8) Aliquat 336.
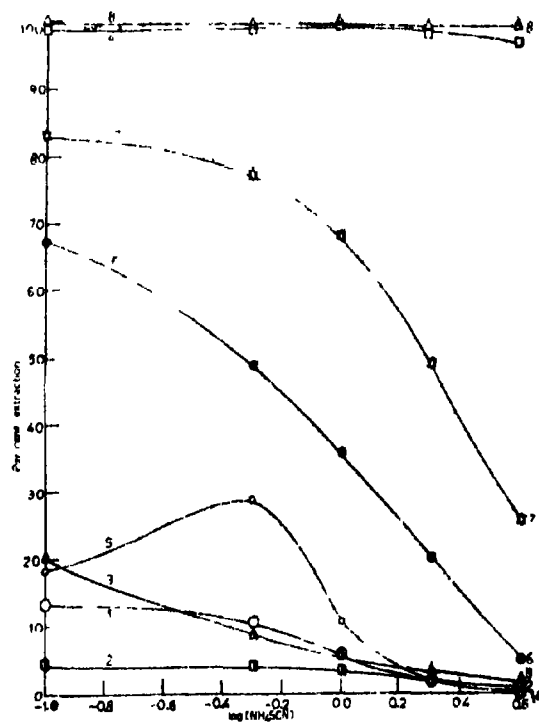
Fig. 3 Extraction of Cd(II) from NH_4SCN solutions by various 0.1*M* amines in chloroform and benzene. Chloroform solvent : (1) Primene JM-T ; (2) Amberlite LA-1 ; (3) Alamine 336 ; (4) Aliquat 336. Benzene Solvent : (5) Primene JM-T ; (6) Amberlite LA-1 ; (7) Alamine 336 ; (8) Aliquat 336.
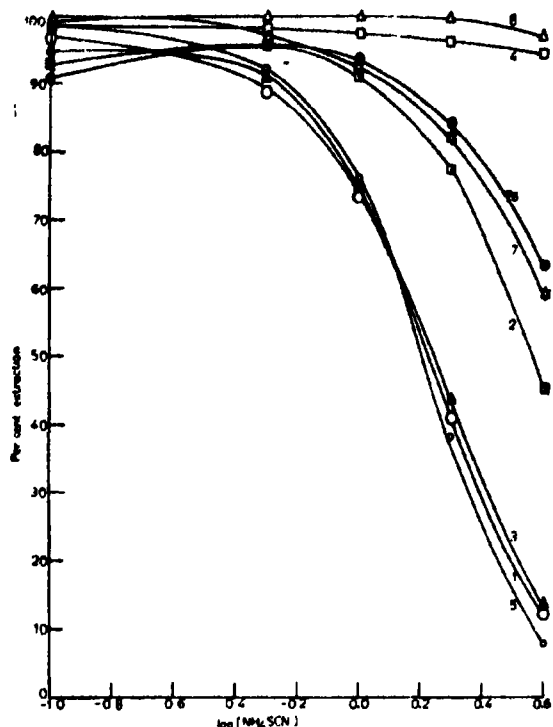
Fig. 4. Extraction of Hg(II) from NH_4SCN solutions by various 0.1*M* amines in chloroform and benzene. Chloroform solvent: (1) Primene JM-T; (2) Amberlite LA-1, (3) Alamine 336; (4) Aliquat 336. Benzene solvent: (5) Primene JM-T; (6) Amberlite LA-1; (7) Alamine 336; (8) Aliquat 336.

different liquid anion exchangers, is shown in Figs. 2,3 and 4, respectively. The extraction of all the three metal ions increases with decreasing thiocyanate concentration with a tendency to attain a limiting value. The effect of *p*H of the aqueous phase on the extractions was found to be negligible within the *p*H range 2.0 to 5.0. The extraction behaviour of these elements is more or less similar to their sorption on solid anion-exchange resins[10]. The extractive power of the various amines for all these elements follows the order:

primary $<$ secondary $\lesssim$ tertiary $<$ quaternary.

It is also apparent from these extraction studies that the extractions with benzene as diluent are, generally, higher than those obtained with chloroform diluent. The extractions of these elements in a particular amine-diluent system are in accordance with the stability[11] of their respective thiocyanate complexes in aqueous solutions i.e. Cd$<$Zn$<$Hg.

Identification of the extracted species:

The stoichiometry of the extracted species has been determined by extraction isotherms, log-log plots of amine concentration versus distribution ratio and analysis of organic extract at maximum loading conditions. The results on extracted species are summarized in Table 1. It is apparent from the results of the various methods employed to determine the nature of the extracting species that there is a fairly good agreement between the results of loading experiments and analysis data. But in some

TABLE 1—RESULTS ON IDENTIFICATION OF EXTRACTING SPECIES IN HMWA

Metal ion	Amine	Species identified by		
		Log-log plot	Extraction isotherm	Analysis of organic extract
Zn^{2+}	Alamine 336	$Zn(SCN)_3^-$ and $Zn(SCN)_4^{2-}$	$Zn(SCN)_4^{2-}$	$Zn(SCN)_4^{2-}$
	Aliquat 336	$Zn(SCN)_3^-$ and $Zn(SCN)_4^{2-}$	$Zn(SCN)_4^{2-}$	$Zn(SCN)_4^{2-}$
Cd^{2+}	Aliquat 336	$Cd(SCN)_4^{4-}$	$Cd(SCN)_4^{2-}$	$Cd(SCN)_4^{2-}$
Hg^{2+}	Alamine 336	$Hg(SCN)_3^-$	$Hg(SCN)_4^{2-}$	$Hg(SCN)_4^{2-}$
	Aliquat 336	$Hg(SCN)_3^-$ and $Hg(SCN)_4^{2-}$	$Hg(SCN)_4^{2-}$	$Hg(SCN)_4^{2-}$

cases the results of these two methods do not agree with those of log-log plots. This anomaly is, generally, attributed to the largely different experimental conditions existing in the two methods. In log-log plots, the metal ion concentration is extremely low ($\leq 10^{-6} M$) whereas a much higher concentration has been used for extraction isotherms. Besides this, varying amine concentration, and higher amine to metal ratios have been used in log-log plots. The possibility of extraction of the different species at the different experimental conditions cannot be ruled out. However, more reliance can be placed on the results of the extraction isotherms because these results are confirmed by the analysis of the organic extract at the maximum loading conditions.

Separations:

In order to explore the thiocyanate-HMWA system for some useful separations, the extraction behaviour of indium(III) and thallium(III) has also been studied under indentical experimental conditions. The best conditions of separation, based on the extraction data are given in Table 2. The efficiency of the different separations is indicated by the separation coefficients listed therein. In most of the cases the metal ion from the organic phase can be stripped by washing it with water or an appropriate concentration of nitric acid.

Extraction of zinc and cadmium thiocyanate complexes in benzene in the presence of tri-n-butyl phosphate and pyridine:

The extraction of zinc(II) and cadmium(II) thiocyanate complexes was studied by tributyl phosphate (TBP) and pyridine, diluted with benzene. The effect of *p*H on extraction was studied at 1.0 *M* NH_4SCN and a fixed concentration of TBP or pyridine. In TBP, the extraction of both the metal ions is almost independent of *p*H within the range 3.0-6.0. However, in the case of pyridine, the extraction increases with increasing *p*H of the aqueous phase and the plots of *p*H versus log D gave straight lines with slopes close to 1 for both the metal ions. At constant concentration of TBP or pyridine the extractions of Zn(II) and Cd(II)

TABLE 2—MUTUAL BINARY SEPARATIONS OF Zn(II), Cd(II), Hg(II), In(III) AND Tl(III) BY VARIOUS AMINES (0 1 *M*) IN CHLOROFORM AND BENZNE

Metal ions separated	Extractant	Molarity of NH_4SCN	Separation coefficient (β)
Zn(II) from Cd(II)	Amberlite LA-1 in chloroform	0 1	3.6×10^{3}
	Alamine 336 in chloroform	0 5	$1\ 3\times10^{3}$
Hg(II) from Cd(II)	Amberlite LA-1 in chloroform	0.5	$4\ 6\times10^{3}$
	Alamine 336 in chloroform	0.5	2.8×10^{3}
Zn(II) from Tl(III)	Aliquat 336 in benzene	0.1 – 4.0	$>10^{4}$
	Aliquat 336 in chloroform	0.1 – 4.0	$>10^{4}$
H (II) from Tl(III)	Aliquat 336 in benzene	0.1 – 4.0	$>10^{4}$
	Aliquat 336 in chloroform	0.1 – 4.0	$>10^{4}$
Cd(II) from Tl(III)	Aliquat 336 in benzene	0.1 – 4.0	$>10^{4}$
	Aliquat 336 in chloroform	0.1 – 4.0	$>10^{4}$
In(III) from Tl(III)	Aliquat 336 in benzene	0.1 – 4.0	$>10^{4}$

increase with increasing concentration of thiocyanate. The plots of log D versus log [NH_4SCN] are linear with slopes around 1, thus suggesting that $[M(SCN)]^+$ species are getting extracted into the organic phase. The existence of $[Zn(SCN)]^+$ and $[Cd(SCN)]^+$ species in aqueous solutions was reported by Chiang and Hsu[12] and Hume *et al*[13].

The dependence of extraction on the concentration of TBP or pyridine was studied at constant NH_4SCN concentration. The log-log plots of extractant concentration versus distribution ratio gave straight lines with slope around 2 and 4 for zinc and cadmium, respectively

On the basis of the above results, the species being extracted are inferred to be $[Zn(SCN).2TBP]^+$, $[Zn(SCN).2py]^+$, $[Cd(SCN)\ 4TBP]^+$ and $[Cd(SCN).4py]^+$. Such species should not be extracted into a non polar medium like benzene, since they are

Fig. 5. Extraction of different metals from aqueous NH_4SCN solutions by 1.0 *M* TBP in benzene.

charged. Therefore, it is assumed that some anion, X^-, is associated to make the species neutral and thus extractable into benzene. For pyridine system, X^- may be either OH^- or ClO_4^- but for TBP system the possibility of OH^- is ruled out because the extractions are almost independent of *p*H. The possibility of ClO_4^- has been suggested because it is present in larger excess in the aqueous phase as perchloric acid has been used for adjusting the *p*H.

Fig. 6. Extraction of different metals from aqueous NH_4SCN solutions by 0.1 *M* pyridine in benzene.

The extraction behaviour of silver(I), manganese(II), cobalt(II), mercury(II) and thallium(III) in addition to zinc(II) and cadmium(II) has been studied as a function of NH_4SCN concentration keeping the concentration of TBP or pyridine constant (Figs. 5 and 6). On the basis of the extraction data it has been possible to achieve some typical separations of analytical and radiochemical interest. The conditions for various separations along with

separation factors are given in Tables 3 and 4. In all the cases, metal ion from the organic phase can be conveniently stripped by washing it with distilled water.

TABLE 3 – SEPARATION OF Zn(II) FROM Ag(I), Mn(II), Co(II), Cd(II), Hg(II) AND Tl(III) FROM NH_4SCN SOLUTIONS BY TBP (1.0 *M*) IN BENZENE

Zn(II) separated from	Molarity of NH_4SCN	Separation coefficient (β)
Ag(I)	0.5	9×10^{3}
Mn(II)	0.05	3.4×10^{3}
Co(II)	0.1	3×10^{3}
Cd(II)	0.05	7.2×10^{3}
Hg(II)	0 5	5×10^{3}
Tl(III)	0 01 – 1.0	$>10^{4}$

TABLE 4—SOME BINARY METAL ION SEPARATIONS FROM NH_4SCN SOLUTIONS BY PYRIDINE (0 1 *M*) IN BENZENE

Metal ions separated	Molarity of NH_4SCN	Separation coefficient (β)
Mn(II) – Co(II)	0.5	$6 6 \times 10^{3}$
Zn(II) – Hg(II)	0.5	2×10^{3}
Zn(II) – Ag(I)	0 5	4×10^{3}
Cd(II) – Ag(I)	0 5	2×10^{3}
Cd(II) – Hg(II)	0 5	2×10^{3}
Cd(II) – Tl(III)	0 1 – 0.5	$>10^{4}$

Conclusion :

The present studies on the extraction of metal ions as thiocyanate reveal that most of the metal ions investigated show negligible extraction in non-oxygenated solvents Some of the metal ions are extracted by oxygenated solvents but the extractions, in general, are not quantitative. High molecular weight amines are better extractants for Zn(II), Cd(II), Hg(II) and In(III) from aqueous thiocyanate solutions. These amine extraction systems are more useful for the separations and provide conditions for metal ion separations like Zn(II)-Cd(II), Cd(II)-Hg(II), Cd(II)-Tl(III), Hg(II)-Tl(III) and In(III)-Tl(III) (Table 2) with high separation factors. The tributyl phosphate system is only useful for the separation of Zn(II) from other metal ions, while the pyridine thiocyanate system is more versatile and offers conditions for a variety of binary metal ion separations, viz., Mn(II)-Co(II), Zn(II)-Hg(II), Zn(II-Ag(I), Cd(II)-Ag(I), Cd(II)-Hg(II) and Cd(II)-Tl(III). To conclude, the thiocyanate-HMWA systems are more versatile and generally provide separations with higher separation factors.

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The Extraction of Chromium(VI) from Mineral Acid Solutions by Trilaurylamine-Oxide

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Extraction of chromium(VI) from hydrochloric, sulphuric, nitric and orthophosphoric acid solutions by trilaurylamine-oxide (TLAO) in chloroform has been studied. The nature of the extracted chromium(VI) species is established

HELLER[1] was the first to point out the possibility of using amine-oxides as extracting agents, but was unable to carry out extraction because the self-synthesised compounds of uranyl nitrate with heterocyclic amine-oxides (pyridine-N-oxide and quinoline-N-oxide) were not soluble in organic solvents. Later, several workers[2-7] exploited the potentialities of these reagents as extractants for several metals. We report in this communication the extraction of chromium(VI) by trilaurylamine-oxide (TLAO) from hydrochloric, sulphuric, nitric and orthophosphoric acid solutions

Experimental

Materials: Chromic acid (E Merck) was used for preparing chromium(VI) stock solution (0 1*M*) Chromium-51 in the form of sodium chromate in isotonic saline solution (15 mCi/mg specific activity) and Chlorine-36 as hydrochloric acid solution (5-25 mCi/g specific activity) were obtained from the Isotope Division, Bhabha Atomic Research Centre, Bombay. Trilaurylamine-oxide (TLAO) was synthesised by the method described by Davies and Hetzer[8]. Its purity was checked by determining the melting point (m.p. 72°) and molecular weight (cryoscopic method) and by identifying the characteristic ir absorption band for N→O at 965 cm^{-1} The sample was kept in dry atmosphere in a desiccator over silica gel and in a refrigerator when not in use.

A Single Channel Analyser SC 600 (ECIL, Hyderabad) coupled with a 3″ Well type scintillation detector (Nuclear Chicago) was used for γ-activity measurements. β-Activities of the solutions were measured with a liquid G.M. counter.

Procedure: Aqueous solutions (10 ml) containing appropriate concentrations of chromic acid, added tracer and mineral acid were equilibrated for 3-5 min with an equal volume of 0 025*M* TLAO in chloroform. The two phases were then separated by allowing the mixture to settle for 5 min and centrifuging, if necessary. Equal aliquots (5 ml) of each phase were used to measure the activities from which the distribution coefficient (k_d) was calculated. No volume change in the aqueous and organic phases was observed after equilibration.

Results and Discussion

Bazinger *et al*[9] reported the extraction of acids by aliphatic amine-oxides as $(R_3N{\rightarrow}O\ H\ O{\leftarrow}NR_3)^+,A^-$ and as $2\ R_3N{\rightarrow}OH^+,A^-$, respectively from low and high acid media. The formation of such salts has been reported[10] in the case of heterocyclic amine-oxides.

The extraction of chromium(VI) (0.001 *M*) with TLAO/chloroform (0 025 *M*) was studied as a function of aqueous phase concentrations of hydrochloric, sulphuric, nitric and orthophosphoric acid solutions. The k_d values are independent of aqueous phase acidity upto 2 *M* in the case of hydrochloric and sulphuric acid solutions and upto 3 *M* with orthophosphoric acid, beyond which a gradual fall is noticed On the other hand the extraction is comparatively much less in nitric acid solutions with a gradual fall in k_d with increasing acidity even in the 0.01-0 1*M* acidity range The decrease in k_d with increasing acidity in all these systems can be explained [by analogy to the U(VI)-HCl-TOAO system[2]] as due to the decrease in the effective amine-oxide concentration by its bonding to the acid or a competitive extraction process in which the anionic part of the acid preferably gets extracted by the amine-oxide (e g $RNOH^+A^-$). The extraction of chromium(VI) is nearly quantitative from hydrochloric acid medium (% extraction =98.80 at ≤ 2 *M* HCl), as compared with sulphuric acid (% extraction =99.80 at ≤ 2 *M* H_2SO_4) and orthophosphoric acid (% extraction =99.85 at ≤ 3 *M* H_3PO_4) solutions. Addition of NaCl, Na_2SO_4, NaH_2PO_4 and $NaNO_3$ to aqueous phases resulted in a significant decrease in extraction, the decrease being in the order $HNO_3 > HCl > H_2SO_4 \approx H_3PO_4$.

The extraction of chromium(VI) as a function of metal concentration [in the concentration range 10^{-3}-10^{-2} mg/ml of Cr(VI)] with TLAO/chloroform (0.025 *M*) was studied. The log-log plot of the equilibrium chromium(VI) concentration in the aqueous phase vs organic phase at initial aqueous phase acidities of 0.1 *M* and 1 0 *M* with respect to HCl, H_2SO_4 and H_3PO_4 gave straight lines of unit slope, indicating that the extracted chromium(VI) species is monomeric in nature. Under the experimental conditions [max. concentration of Cr(VI) employed is 5.2×10^{-2} mg/ml], chromium(VI) exists predo-

TABLE 1—DATA ON THE COMPOSITION OF THE ORGANIC PHASES OBTAINED AFTER EXTRACTION OF CHROMIUM(VI) FROM HCl SOLUTIONS WITH 0.025 *M* TLAO

Initial aqueous phase (*M*)		Equilibrium organic phase (*M*)			Molar ratio organic phase
[Cr(VI)]	[HCl]	[Cr(VI)]	[(Cl^-)]	[Cl^-] (Blank)	TLAO : Cr(VI) : Cl^-
0.03	0.05	0.0250	0.0250	0.0244	1 : 1 : 0.024
0.03	0.10	0.0250	0.0260	0.0244	1 : 1 : 0.024
0.03	0.30	0.0250	0.0295	0.0248	1 : 1 : 0.188
0.03	0.50	0.0250	0.0348	0.0255	1 : 1 : 0.372
0.03	1.00	0.0250	0.0440	0.0260	1 : 1 : 0.720
0.03	2.00	0.0250	0.0450	0.0265	1 : 1 : 0.740
0.04	1.00	0.0250	0.0440	0.0260	1 : 1 : 0.720
0.05	1.00	0.0250	0.0440	0.0260	1 : 1 : 0.720

minantly as monomeric oxyanion[11] i.e. $HCrO_4^-$ in the aqueous phase. Therefore the extraction of chromium(VI) as protonated oxyanion can be envisaged. This is in conformity with the observation that other elements which form oxyanions in their highest oxidation states are extracted as protonated oxyanions [e.g W(VI) [2], Mo(VI)[12], Re(VII)[13] and Tc(VI)[14]] by oxygen donor extractants

Fig. 1. Variation of the distribution coefficient (k_d) for chromium(VI) (5.2×10^{-3} mg/ml) in hydrochloric, sulphuric and orthophosphoric acid solutions as a function of TLAO concentration in chloroform.

The log-log plots of k_d vs (TLAO) (Fig. 1b) from invariable concentrations of sulphuric and orthophosphoric acid solutions (0.1*M*, 0.5*M* and 1.0*M*) gave a square law k_d dependence on the amine-oxide, irrespective of the acid concentration indicating the formation of disolvates. On the other hand, the slope analysis of the distribution data in hydrochloric acid system (Fig. 1a) indicates that the solvation number depends on the concentration of the acid. At low acid concentration the slope of the log k_d vs log (TLAO) plot shows that the solvation number is close to unity (1.05 at 0.1*M* HCl). As the concentration of the acid in the aqueous phase is increased, the stoichiometric ratio of the components in the organic phase increases gradually, indicating that different extraction mechanisms are operating probably due to the formation of a mixture of solvated chromium(VI) species. The extraction of chloride as a function of aqueous hydrochloric acid concentration (0.25-2.0 *M*) in the presence of chromium(VI) (0.03 *M*) was studied with TLAO/chloroform (0.025 *M*), using ^{36}Cl as radiotracer. The concentration of chloride in the organic phase increased with increasing acidity (Table 1) indicating that the extracted chromium(VI) is a mixture of species containing predominantly $HCrO_3Cl$ at higher acidities. The extraction of protonated chromium(VI) species from mineral acid solutions by oxygen donor solvents TBP[15,16] and TOPO[17] was earlier reported. The existence of such species in aqueous acid systems at high acidities (> 2 *M*) was also reported by several workers[18,19].

The observed Cr : TLAO mole ratio of 2, from sulphuric, nitric and orthophosphoric acid solutions could be explained as arising from the extraction of chromium(VI) species in the form of $2\,R_3NO.H_2CrO_4$. On the other hand, the alteration of mole ratio from hydrochloric acid solutions with increasing acidity suggests extraction of a mixture of chromium(VI) species in the form of $R_3NO.H_2CrO_4$ and/or $R_3NO.HCrO_3Cl$ at higher acidities (> 0.1 *M*) and as $R_3NO\,H_2CrO_4$ at lower acidities (< 0.1 *M*).

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Cation Exchange Chromatographic Separation of Manganese in Mixed Solvent Systems

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Cation exchange chromatographic behaviour of manganese(II) on Dowex 50W-X8 was studied in mixed solvent systems. Methanol, ethanol, 2-propanol, acetone, dioxane and tetrahydrofuran in conjunction with 2 *M* hydrochloric acid were used as eluants.

Amongst the non-aqueous solvents tested, acetone, methanol and ethanol proved to be efficient while 2-propanol, dioxane and tetrahydrofuran had no practical utility. The separation of manganese from binary mixture containing alkali metals, alkaline earth metals and some other associated elements was carried out by the process gradient elution as well as selective elution using combinations of different organic solvents. Similarly, separation of multicomponent mixtures of six elements commonly associated with manganese was done by sequential separation in the mixed solvent system.

ALTHOUGH cation exchange chromatographic[1] behaviour of manganese was studied on Dowex 50W-X8, such studies in the mixed solvent systems are lacking.

The exchange constant in methanol and ethanol media was determined[2] on cationite KU-2 The separation of manganese from nickel[3] was effected using this information Similarly, manganese was separated from copper in acetone-hydrochloric acid solutions[4]. The cation exchange studies for manganese, cobalt and magnesium[5] was carried out in mineral acids containing alcohols. Manganese was separated from nickel[6] with glycine. However, cation exchange separations of manganese in mixed solvent systems such as methanol, ethanol, 2-propanol, acetone, dioxane and tetrahydrofuran are lacking This paper presents such studies. Various interesting separations have also been achieved and reported

Experimental

Apparatus and reagents :

The ion-exchange column (1.4×20 cm) was similar to the one described earlier[7]. A digital *p*H meter (ECIL India, type *p*H-822) with glass and calomel electrodes was used.

A stock solution of manganese was prepared by dissolving 4.5 g of manganese chloride tetrahydrate in 250 ml distilled water containing 1% hydrochloric acid. It was standardized complexometrically[8], and was found to contain 5.10 mg/ml of manganese. Dowex 50W-X8 (Dow Chemical Co, Midland, Mich., U.S.A) 20-50 mesh (H^+ form) was used.

General procedure :

(a) *Procedure for cation exchange studies :* An aliquot of the stock solution, containing 10-20 mg of manganese, was sorbed on the column at flow rate

TABLE 1—CATION EXCHANGE STUDIES OF MANGANESE WITH MINERAL ACIDS AS ELUANT

Eluant (*M*)		Peak elution volume V_{max}, ml	Total elution volume V_t, ml	Manganese recovery (%)	Elution constant (E)	Volume distribution coeff (D_v)	Weight distribution coefficient (D_w)
HCl	1	–	200	19 8	–	–	–
	2	75	200	100.0	0.58	1 74	1.21
	3-4	50	150	100 0	1 08	0 93	0.65
HNO_3	1	–	200	17 4	–	–	–
	2	100	225	100 0	0 39	2 55	1 77
	3	75	175	100 0	0.58	1.74	1 21
	4	50	150	100.1	1 08	0 93	0 65
H_2SO_4	1	–	200	83.9	–	–	–
	2	50	150	100.1	1 08	0.93	0.65
	3-4	50	100	100.0	1.08	0.93	0.65
$HClO_4$	1	–	200	88 4	–	–	–
	2	100	200	100.0	0.39	2.55	1.77
	4	75	175	100.1	0.58	1.74	1.21

TABLE 2—CATION EXCHANGE STUDIES OF MANGANESE(II) IN MIXED SOLVENT SYSTEMS

Mn(II) 10.2 mg   Weight of resin = 12 55 g   Column = 1.4×20 cm   Resin = Dowex 50 W – X8 (H^+ form)

Organic solvents m (%) with 2 *M* HCl	Peak elution volume V_{max}, ml	Total elution volume V_t, ml	Manganese recovery (%)	Elution constant (E)	Volume distribution coefficient (D_v)	Weight distribution coefficient (D_w)
Methanol						
20	75	250	100.00	0 58	1 74	1.21
40	75	275	100 19	0 58	1 74	1 21
60	100	300	98 80	0 39	2 55	1.77
80	100	300	93.66	0 39	2.55	1.77
Ethanol						
20	75	250	100 05	0 58	1 74	1 21
40	75	275	99 84	0 58	1 74	1.21
60	100	300	97 06	0.39	2 55	1 77
80	100	300	84 66	0 39	2 55	1.77
2-Propanol						
20	75	250	100 00	0 58	1.74	1.21
40	75	275	99 82	0 58	1 74	1.21
60	100	300	85 17	0 39	2.55	1 77
Acetone						
20	75	250	100 00	0.58	1 74	1.21
40	75	275	100.00	0·58	1 74	1 21
60	100	300	99 95	0.39	2 55	1 77
80	50	225	100 01	1.08	0.93	0.65
1,4-Dioxane						
20	75	250	100 00	0 58	1 74	1 21
40	75	275	99 22	0 58	1 74	1.21
60	50	300	98 36	1.08	0.93	0 65
Tetrahydrofuran						
20	75	250	100.28	0 58	1 74	1.21
40	75	275	99.15	0 58	1.74	1.21
60	100	300	98 07	0 39	2.55	1.77
80	50	250	92 57	1.08	0 93	0.65
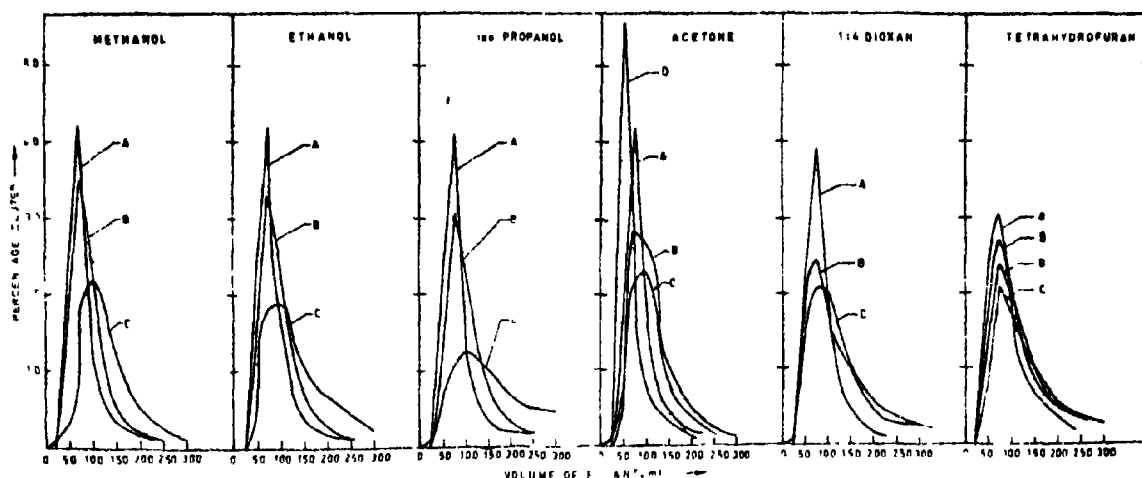
Fig. 1. Elution behaviour of manganese(II) on Dowex 50W-X8 with various mixed solvent systems. A . 2 *M* HCl in 20% non-aqueous solvent ; B : 2 *M* HCl in 40% non-aqueous solvent , C 2 *M* HCl in 60% non-aqueous solvent ; D : 2 *M* HCl in 80% non-aqueous solvent.

of 1 ml/min. The column was washed with water. Manganese from the column was eluted with various mineral acids (Table 1) and wi h mixtures of 2 *M* hydrochloric acid with various concentrations of non-aqueous solvents like methanol, ethanol, acetone, 2-propanol, dioxane or tetrahydrofuran (Table 2 ; Fig. 1). The effluent lot was collected in 25 ml fractions and in each case ten to twelve fractions were collected. The fractions were evaporated almost to dryness prior to the determination of manganese by complexometric titration[8].

(b) *Procedure for separations* : An aliquot of solution containing mixture of two or more cations along with manganese was passed on the column at the flow rate of 1 ml/min. The specific eluants as described under various separations, were then passed through the column to elute each element at the flow rate of 2 ml/min. The concentration of a particular element in the eluted solutions was determined quantitatively by an appropriate method, usually involving complexometric titration.
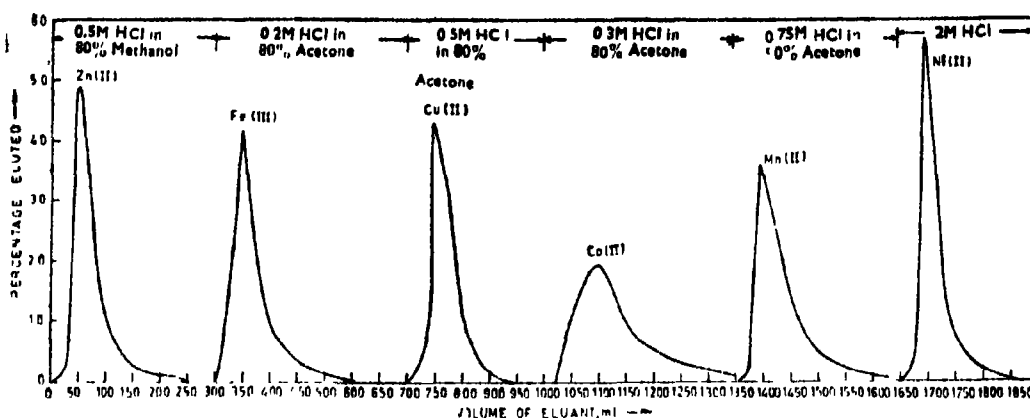
Fig. 2. Sequential separation of zinc, iron(III), copper(II), cobalt(II), manganese and nickel.

0.5 *M* HNO_3(1) 0.3 *M* HCl in 90% Acetone(2) 1 *M* HCl 90% Acetone(3) 2 *M* HCl in 40% Ethanol(4) 1.5 *M* HCl H_2SO_4(5)
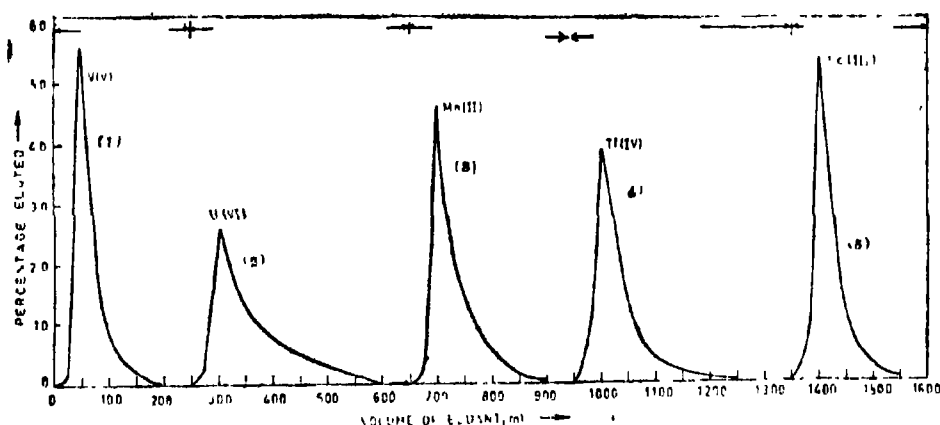
Fig. 3. Sequential separaton of vanadium(V), uranium(VI), manganese(II), titanium(IV) and scandium(III).

0.5 *M* HCl in 60% Propanol(Cd) 0.5 *M* HCl 80% Acetone(Pb) 2 *M* HCl in 80% Acetone(Mn) 3 *M* HCl in 60% Methanol(Al) 3*M* HCl(Ca)
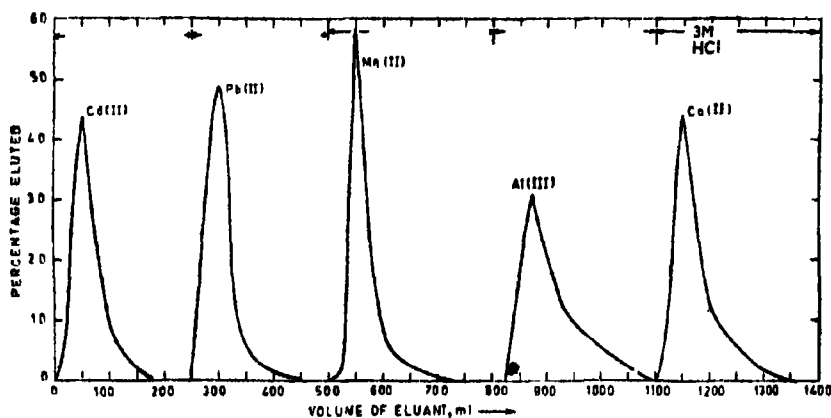
Fig. 4. Sequential separation of cadmium, lead(II), manganese(II), aluminium and calcium.

Results and Discussion

The elution constant (E) and distribution coefficients (D_v, D_w) were evaluated as described earlier[1]. From their knowledge, it was possible to have selectivity scale for mineral acids as eluants, as well as for non-aqueous solvents mixed with 2 *M* hydrochloric acid. The scale was H_2SO_4 > HCl > HNO_3 > $HClO_4$ for mineral acids and acetone > ethanol > methanol > 1,4-dioxane > tetrahydrofuran > 2-propanol for non-aqueous solvents.

Amongst the eluants tested for manganese the complexing organic acids were found to be poor[1]. The mineral acids in the concentration range of 0 to 1 *M* were poor eluants, but at 2 *M* acidity elution was quantitative for all acids with the exception of perchloric acid. The optimum concentration of mineral acid was 2 *M*. The most practical eluant was hydrochloric acid. Hence it was used in all investigations along with non-aqueous solvents. A lower concentration of hydrochloric acid could be used provided it was used in conjunction with non-aqueous solvents.

There are several advantages of carrying out cation exchange chromatographic separations in mixed solvent systems as described earlier[7]. Among the various non-aqueous solvents used, it was noted that acetone was the most promising because the elution of manganese was quantitative with 20 to 80% acetone in 2 *M* hydrochloric acid. Ethanol and methanol were the next best from the view point of separation. With 2-propanol the flow rate was extremely low at higher concentrations. Though it was possible to get the separation with 1,4-dioxane, the problem of two phase formation was encountered. With tetrahydrofuran system, the extraction was not generally quantitative in higher concentration. Further, it was possible to elute manganese quantitatively with 0 75 to 2 *M* hydrochloric acid, only in the presence of 80 to 90% acetone. The methanol and ethanol system was effective for separation of multicomponent mixtures.

During ion exchange separation, it was noted that manganese was strongly bound to the resin in comparison to other elements and was therefore eluted later in certain separations. In the few instances where manganese was weakly bound to the resin, it was eluted first before elution of interfering ion and was thus separated in mixture. Few such separations are illustrated in the following part.

Separation of manganese in acetone media: Vanadium(V), mercury(II), indium(III), bismuth(III) and lithium were separated from manganese in acetone media by selective elution of these ions as they were weakly bound. On passing a binary mixture of manganese with any of these ions on the column, they were taken up by the resin. They were first eluted with 0.5 *M* hydrochloric acid, followed by the elution of manganese with 2 *M* hydrochloric acid in 80% acetone. Zinc and cadmium were separated from manganese by first eluting zinc and cadmium with 0.5 *M* hydrochloric acid in 80% methanol, with subsequent elution of manganese with 2 *M* hydrochloric acid in 80% acetone.

Uranium(VI), iron(III), cobalt(II), copper(II), gallium(III) and lead(II) were separated from manganese by eluting these elements with 0.5 *M* hydrochloric acid in 80% acetone [0.5 *M* hydrochloric acid in 90% acetone for uranium(VI) and cobalt(II)], with subsequent elution of manganese with 2 *M* hydrochloric acid in 80% acetone.

TABLE 3—ION EXCHANGE SEPARATION OF MANGANESE(II) FROM VARIOUS OTHER ELEMENTS IN BINARY MIXTURES

Mn(II) = 5 1 mg

Foreign ion	Amount added mg	Manganese found mg	Recovery of manganese (%)	Eluant for other elements	Eluant for manganese
V(V)	50 00	5.0	98 0	0.5 *M* HCl	2 *M* HCl in 80% acetone
Hg(II)	35 00	5 1	100 0	,,	,,
In(III)	54.00	5.1	100 0	,,	,,
Bi(III)	65.00	5 1	100.0	,,	,,
Li	50.50	5 1	100.0	,,	,,
Fe(III)	62 40	5 1	100 0	0 5 *M* HCl in 80% acetone	,,
Zn(II)	65 20	5 1	100 0	0 5 *M* HCl in 80% methanol	,,
Cd(II)	60.50	5 1	100.0	,,	,,
U(VI)	45.30	5.1	100 0	0 5 *M* HCl in 90% acetone	,,
Co(II)	12 00	5 0	98 0	,,	,,
Cu(II)	65 00	5 1	100.0	0.5 *M* HCl in 80% acetone	,,
Ga(III)	45.00	5 1	100 0	,,	,,
Pb(II)	56.30	5.1	100.0	,,	,,
Na	45.00	5 0	98.0	4 *M* HCl	0 75 *M* HCl in 90% acetone
K	50.00	5.1	100.0	,,	,,
Rb	40.40	5 1	100 2	,,	,,
Cs	45.40	5 0	99.1	,,	,,
Be	30.40	5 1	100 0	,,	,,
Ca	65 00	5.1	100 0	,,	,,
Mg	50.40	5.1	100 0	,,	,,
Al	65.30	5.1	100.0	,,	,,
Ti(IV)	45.00	5.1	100.0	8 *M* HCl	,,
Ni(II)	45.30	5.0	98 0	4 *M* HCl	,,
Sc(III)	50.00	5.1	100.0	8 *M* HCl	3 *M* HCl in 60% ethanol
Y(III)	50.00	5 1	100.0	,,	,,
Zr(IV)	50 40	5 1	100.0	,,	,,
Th(IV)	60.80	5.1	100.0	,,	,,
Ce(III)	60.40	5.1	100.0	,,	,,
Sr(III)	60.00	5.1	100.0	,,	,,
Ba(II)	65.40	5.1	100.0	,,	,,

In contrast, in acetone media some elements were taken up strongly by the resin and were eluted later. Manganese was separated from sodium, potassium, rubidium, caesium, beryllium, calcium, magnesium, aluminium, titanium(IV) and nickel(II) by its elution with 0.75 *M* hydrochloric acid in 90% acetone, followed by elution of all the listed ions with 4 *M* hydrochloric acid. In case of titanium it was necessary to use 8 *M* hydrochloric acid (Table 3).

Separation in ethanol media : Since scandium(III), yttrium(III), zirconium(IV), thorium(IV), cerium(III), strontium(III) and barium(II) were strongly retained on the resin in comparison to manganese, the latter was first eluted with 3 *M* hydrochloric acid in 60% ethanol, followed by elution of all the elements with 8 *M* hydrochloric acid (Table 3).

Separation of manganese from multi-component mixtures : Manganese was separated from several multicomponent mixtures in the following manner :

A mixture of zinc, iron(III), copper(II), cobalt(II), manganese(II) and nickel(II) was sorbed on the column. Zinc was first eluted with 0.5 *M* hydrochloric acid in 80% ethanol, then iron(III) was eluted with 0.2 *M* hydrochloric acid in 80% acetone, copper(II) with 0.5 *M* hydrochloric acid in 80% acetone, cobalt(II) with 0.3 *M* hydrochloric acid in 90% acetone, manganese with 0.75 *M* hydrochloric acid in 90% acetone and finally nickel(II) was eluted with 2 *M* hydrochloric acid.

A mixture of vanadium(V), uranium(VI), manganese(II), titanium(IV) and scandium(III) was sorbed on the column. Vandadium(V) was eluted with 0.5 *M* nitric acid, uranium(VI) with 0.3 *M* hydrochloric acid in 90% acetone, manganese with 1 *M* hydrochloric acid in 90% acetone, titanium(IV) with 2 *M* hydrochloric acid in 40% ethanol and finally, scandium(III) was eluted with 1.5 *M* sulphuric acid.

A mixture of cadmium(II), lead(II), manganese(II), aluminium and calcium was passed on the column. Cadmium was eluted with 0.5 *M* hydrochloric acid in 60% 2-propanol, lead(II) with 0.5 *M* hydrochloric acid in 80% acetone, manganese with

0.5 *M* HCl in 80% Acetone | 1 *M* HCl in 90% Acetone | 3 *M* HCl in 40% Ethanol | 3 *M* HNO_3
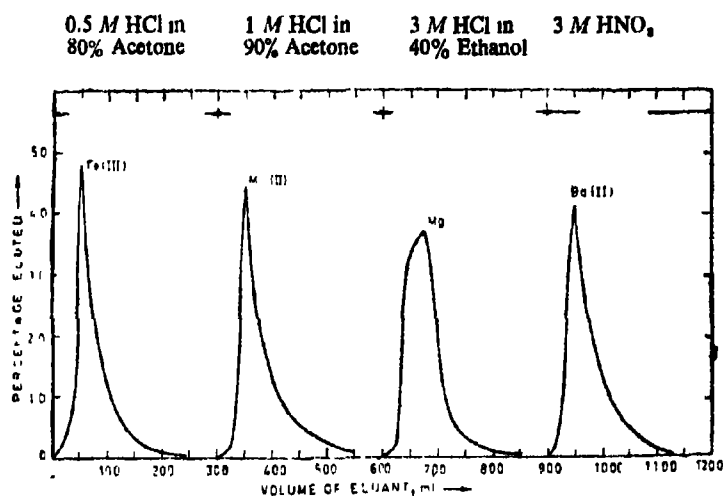
Fig. 5. Sequential separation of iron(III), manganese(II), magnesium and barium(II)

TABLE 4—SEPARATION OF MANGANESE FROM MULTICOMPONENT MIXTURES

Sl No.	Element	Amount added mg	Amount found mg	Recovery %	Eluant
1.	Zn(II)	10.00	10.00	100.00	0.5 *M* HCl in 80% methanol
	Fe(III)	9.20	9.20	100 00	0.2 *M* HCl in 80% acetone
	Cu(II)	10.06	9 90	99.00	0.5 *M* HCl in 80% acetone
	Co(II)	8.80	8.70	98.86	0.3 *M* HCl in 90% acetone
	Mn(II)	10.20	10 10	99.01	0.75 *M* HCl in 90% acetone
	Ni(II)	9.40	9.40	100.00	2 *M* HCl
2.	V(V)	10.00	10.00	100.00	0.5 *M* HNO_3
	U(VI)	9 80	9.70	98.98	0.3 *M* HCl in 90% acetone
	Mn(II)	10 20	10.20	100.00	1 *M* HCl in 90% acetone
	Ti(IV)	9.60	9.50	98.96	2 *M* HCl in 40% ethanol
	Sc(III)	10.00	10.00	100.00	1.5 *M* H_2SO_4
3.	Cd(II)	10.00	10.00	100.00	0.5 *M* HCl in 60% 2-propanol
	Pb(II)	10.30	10.20	99.02	0.5 *M* HCl in 80% acetone
	Mn(II)	10.20	10.20	100.00	2 *M* HCl in 80% acetone
	Al(III)	9.40	9.40	100.00	3 *M* HCl in 60% methanol
	Ca(II)	10.50	10.40	99.05	3 *M* HCl
4.	Fe(III)	9.20	9.20	100.00	0.5 *M* HCl in 80% acetone
	Mn(II)	10.20	10.20	100.00	1 *M* HCl in 90% acetone
	Mg(II)	10.00	9.90	99.00	3 *M* HCl in 40% ethanol
	Ba(II)	10.40	10.30	99.03	3 *M* HNO_3

2 *M* hydrochloric acid in 80% acetone, aluminium with 3 *M* hydrochloric acid in 60% methanol and finally calcium with 3 *M* hydrochloric acid.

A mixture of iron(III), manganese(II), magnesium and barium was passed on the column and elution was carried out for iron(III) with 0 5 *M* hydrochloric acid in 80% acetone, manganese(II) with 1 *M* hydrochloric acid in 90% acetone, magnesium with 3 *M* hydrochloric acid in 40% ethanol and finally, barium with 3 *M* nitric acid (Table 4 ; Fig. 5).

In all the above separations the total volume of the eluant used was 250 ml. Invariably, the analysis of elements was done by complexometry with the exception of alkali and alkaline earth elements which were determined by flame emission spectroscopy.

The separation of manganese from iron(III), cobalt(II), nickel(II), vanadium(V), titanium(IV), aluminium and lead(II) was significant as these are associated with it in alloys. The isolation of manganese from iron(III) and barium was important as it occurs with them in minerals.

The overall separations required 3 to 4 hr. The relative standard deviation was ±1.5%.

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Determination of Zinc with Cupric Ion-Selective Electrode and its Analytical Application in Fertilizers

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The results of potentiometric titration of Zn(II) with cupric ion-selective electrode in the presence of ammonia buffer solution are recorded. The best results for determination of Zn(II) are obtained in 0.1 *M* ammonia buffer. Samples containing 1.5 μmoles in 5 ml to 6 μmoles in 10 ml solution could be analysed. Results compare favourably with other methods.

The application of the method for determination of zinc in fertilizers is demonstrated.

ONE of the main advantages of ion-selective electrode used in the potentiometric titrations lies in the development of indirect methods for determination of such anions or cations which themselves are not sensor of electrodes[1-3].

In the course of our investigation with ion-selective electrode we tried to apply the method of Baumman and Wallace[1] for indirect determination of Zn(II) using cupric ion-selective electrode. However, the results obtained proved to be quite unsatisfactory. An equivalent part of the titration curve could not be obtained.

If α-coefficient of the Zn(II) and Cu(II) side reactions in ammonia buffer[4] are taken into consideration, one could arrive at the conclusion that the inequality $K'_{Zn-EDTA} > K'_{Cu-EDTA}$ remains valid ($K'_{Zn-EDTA}$ and $K'_{Cu-EDTA}$ are the adequate conditional constants). The chemical equilibrium accounting for the inflection point, which coincides with the equivalent point is presented in the reaction.

$$Zn^{2+} + \text{Cu-EDTA} = \text{Zn-EDTA} + Cu^{2+} \quad \dots (1)$$

In an acidic medium where $K'_{Zn-EDTA} < K'_{Cu-EDTA}$, more of indicator Cu-EDTA might prove necessary for the reaction[1] and the curve is not well defined.

In ammonia medium, where $K'_{Zn-EDTA} > K'_{Cu-EDTA}$, a single drop of indicator Cu-EDTA is enough for the displacement of cupric ions.

Experimental

Apparatus : All measurements were made using Seibold Cupric Ion Activity Electrode, Model 29-17, Ag/AgCl double junction reference electrode with 0.1 *M* KNO_3 in the outer compartment and the Seibold Model G 104 digital *p*H/mV meter. A glass electrode with the same reference was used to ascertain *p*H of the solutions.

Reagents : The indicator Cu-EDTA was prepared according to the reported method[3]. The final solution contained 0.5 *M* Cu-EDTA with *p*H 4.09. The titrant, 0.1 *M* Na_3HEDTA was prepared from 0.1 *M* $Na_2H_2EDTA.2H_2O$ and 0.1 *M* NaOH. Buffer solution NH_4^+/NH_3 with concentrations 1 *M*, 0.1 *M* and 0.05 *M* were used for keeping the *p*H constant between 7.5 and 8. Ammonium nitrate containing microamount of zinc as ZnO was used. $Zn(NO_3)_2$ and $Cu(NO_3)_2$ were added to the impure carbamide.

Determination of Zn(II) in solutions : The diluted solution of zinc (10^{-3} *M*) in ammonium medium was prepared just before the determination. An aliquot (3.00 to 10.00 ml) was drawn from this solution and transferred into a plastic beaker One drop of 0.5 *M* indicator Cu-EDTA was added. The electrodes were immersed into the solution and the solution titrated with 0.01 *M* Na_3HEDTA A microburette of 2.000 ± 0.005 ml was used. The rate of titration was 0.01 ml/10 sec with constant stirring (50 rev/min).

Determination of Zn(II) in fertilizers : To a sample containing ~1.0 g NH_4NO_3 or 0.5 g $CO(NH_2)_2$ were added 1-2 drops of HNO_3 (1 : 1) and 10.0 ml 1 *M* ammonia buffer. The mixture was diluted with double distilled water up to the mark. An aliquot of 5.00 ml was titrated in the presence of 1 drop of Cu-EDTA indicator with the cupric ion-selective electrode.
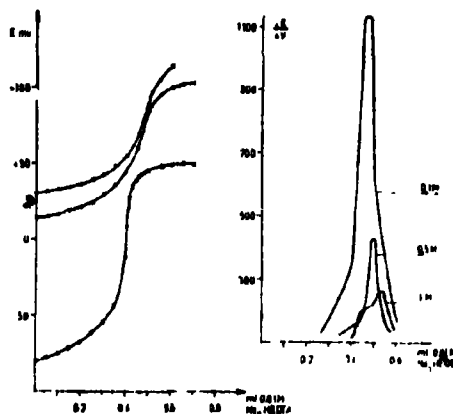
Fig. 1. Zn(II) titration with Cu-selective electrode at different concentration of the buffer [7.00 ml Zn(II) 0.563.10^{-3}*M*].

TABLE 1—REPRODUCIBILITY AND ACCURACY OF THE RESULTS OBTAINED FROM POTENTIOMETRIC TITRATION OF Zn(II) WITH CUPRIC ION-SELECTIVE ELECTRODE, USING Cu-EDTA AS INDICATOR

Buffer concentration M	Zn(II) Taken μ moles	Mean, $\bar{x}$ μ moles	$d_i = \frac{\Sigma(\bar{x}-x_i)}{n}$	$S_{\bar{x}} = \frac{\sqrt{\Sigma(x-x_i)}}{n-1}$	$\%S = \frac{S_{\bar{x}}}{x}-0.100$
0.1	3.94	4.02	0.085	0.0106	0.26
0.5	4 26	4.33	0.121	0 1634	3.77
0.2	1.22	1.17	0.116	0.133	11 4

Results and Discussions

The effect of concentration of the buffer solutions on the titration of Zn(II) is shown in Fig 1 Statistical analyses of some of the results are presented in Table 1. It is shown that the concentration of the buffer solution of 0.1 M is the best medium for the titration.

TABLE 2—THE EFFECT OF INTERFERING IONS ON THE DETERMINATION OF Zn(II) BY POTENTIOMETRIC TITRATION WITH CUPRIC ION-SELECTIVE ELECTRODE

Interfering ions, M	M/Zn	Zn(II) μ moles Obtained	Taken
K^+	120	3.94	3 94
Ca^{2+}	120	3.93	3.94
SO_4^{2-}	120	3 95	3 94
Cl^-	100	3 95	3 94
NO_3^-	100	3 95	3 94
Ba^{2+}	100	3.96	3 94
$CO(NH_2)_2$	100	3.96	3 94

Fig 2. Determination of Zn(II) in fertilizers with Cu-selective electrode in 0.1M ammonia buffer solution ; Curve 1—Zn(II) in NH_4NO_3 and Curve 2—Zn(II) in $CO(NH_2)_2$.

The effect of interferring ions on the equivalence point of titration curves are shown in Table 2. 120 times SO_4^{2-} ion, present in excess does not affect the result using Cu electrode, but using Cd electrode[4], only 10 times SO_4^{2-} excess is tolerated.

TABLE 3—STATISTICAL ANALYSES OF THE RESULTS OF DETERMINATION OF Zn(II) IN FERTILIZERS

Statistical analyses	Zn(II) in NH_4NO_3 %	Zn(II) in $CO(NH_2)_2$ mol/l $\times 10^6$
mean, x	0 995	0.560
$d_i = \frac{\Sigma(x-x_i)}{n}$	0 0008	0.002
$\%d_i = \frac{\bar{d}_i}{x} . 100$	0 084	0 036
$S_{\bar{x}} = \frac{\sqrt{\Sigma(x-x_i)}}{n-1}$	0 001	0 0025
$\%S = \frac{S_x}{x}$ 100	0 1	0.045
$1/4S_{\bar{x}}$	0.00015	0 0006

The application of the method for determination of Zn(II) in fertilizers is shown in Fig. 2 and Table 3 Complexometric titration and atomic absorption were used as comparative methods.

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Floatable Ion Associates Formed in the System Iridium(III)-Tin(II)-Chloride-Basic Dye

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Sparingly soluble (in aqueous solutions) ion associates of polyvalent anionic iridium complexes, formed in hydrochloric acid medium containing tin(II) with basic dyes (rhodamine 6G, malachite green or crystal violet) collect on the phase boundary or on the walls of the separatory funnel, when shaken with solvents of low polarity. The separated floatation compounds dissolve in polar solvents. Optimum conditions for complete floatation of iridium compounds are found Molar ratios (Ir : Sn : dye) in these compounds are determined spectrophotometrically and suitable formulae are proposed.

ANIONIC complexes of many elements with appropriate ligands, formed with basic dye ion associates (ion pairs), and having a molar ratio anion : basic dye=1 : 1, are extracted by nonpolar solvents. This has been utilized for a long time in extraction-spectrophotometric methods for determination of elements[1,2]. Some ion associates with basic dyes are not extracted when the aqueous phase is shaken with solvents of low polarity, but collect at the phase boundary or on the walls of the separatory funnel. In this case the anions are polyvalent and the number of monovalent cations of the dye in ion associates is more than one (2 to 5). This process is some kind of floatation of sparinglysoluble ion associate without participation of a surface active substance, usually added in typical floatation process. Precipitates separated from aqueous and organic solvent phases and washed are soluble in some polar solvents. The solutions obtained can form a basis of very sensitive, so called, floatation-spectrophotometric methods[3].

It is known that most of the platinum metals form polyvalent anionic complexes in hydrochloric acid medium in presence of tin(II)[4-6], forming mixed complexes with Cl^- and $SnCl_3^-$ ligands. This work is devoted to a study of ion associates given by such complex of iridium with some basic dyes.

Experimental

Apparatus and Reagents :

A Specord UV-VIS recording and a VSU-2P spectrophotometer with 1 cm cells were used for absorbance measurements. Standard iridium solution (1 mg/ml) was prepared by dissolving 0.5970 g of iridium(III) chloride (Koch-Light) in 2 *M* HCl with the addition of 5 ml of 5% NaCl solution. The solution was standardized gravimetrically with thionalide[7]. Working solutions were prepared by diluting with 2 *M* HCl.

Radioisotope ^{192}Ir, ammonium hexachloroiridate(IV) in 0.1 *M* HCl was employed. The dyes were purified by precipitation from ethanolic solutions by addition of a 5-fold excess of diethyl ether. The strength of the dye solutions was rhodamine 6G (R6G) 2×10^{-3} *M* (approx. 0.1%), malachite green (MG) and crystal violet (CV) 1×10^{-3} *M* (about 3.6×10^{-2}% and 4.0×10^{-2}%, respectively). Stannous chloride was used as 10% solution of $SnCl_2.2H_2O$ in 2 *M* HCl.

Procedure :

An acid (HCl) solution containing 10 μg of iridium is evaporated to dryness on a boiling water bath. Suitable volumes of $SnCl_2$ solution and HCl are added to obtain the appropriate acidity. The solution is heated on a boiling water bath for 10-15 min, allowed to cool to room temperature, transferred to a separatory funnel, the dye solution is added, volume made upto 20 ml and the acidity is adjusted. 5 ml of floating organic solvent is then added and shaken for 1 min. The water and organic phases are separated carefully and precipitate is washed and dissolved in the polar solvent. The absorbance of the solutions is measured at 530 nm in the case of the system with R6G, at 627 nm with MG, and at 595 nm with CV, against reagent blanks prepared in the same way

Results and Discussion

Preliminary studies :

Preliminary experiments were carried out to find the basic dyes, which would form floatable ion associates with anionic iridium complex formed in $SnCl_3^-$-HCl medium. The tests involved xanthene, triphenylmethane and azine dyes, commonly used in analytical chemistry[1,2]. The acidity in these experiments was fixed from 0.5 to 6 *M* HCl. A 30-60 fold molar excess of the basic dye with respect to iridium (10 μg) was used. The aqueous solutions were shaken with di-isopropyl ether, benzene toluene and chloroform.

Only ion associates of the anionic iridium complex with rhodamine 6G, malachite green and crystal violet are floated. The sparingly soluble compounds collect on the phase boundary or on the walls of the separatory funnel.

Conditions of the floatation :

The floating solvents appeared the best are di-isopropyl ether for the ion associates of iridium with rhodamine 6G and malachite green and benzene for ion associate with crystal violet. In these systems, the sparingly soluble compounds accumulate on the walls of the separatory funnel.

The phase volume ratio has no effect on complete separation of the iridium as ion associate. The iridium in separated compounds and in solutions was determined radiometrically. A relatively long shaking of phases in separatory funnel (about 1 min) is necessary. The best concentration of HCl in the aqueous phase during the floatation is 0.4-0.6 *M*, 2.0-2.4 *M* and 2.3-2.7*M* for malachite green, crystal violet and rhodamine 6G, respectively.

For the complete separation of iridium during a floatation process in the form of a sparingly soluble ion associate, a 55-fold molar excess of rhodamine 6G (with respect to iridium) is necessary. In the cases of malachite green and crystal violet, these molar excesses are 60 and 12, respectively. These dependences are shown in Fig. 1.
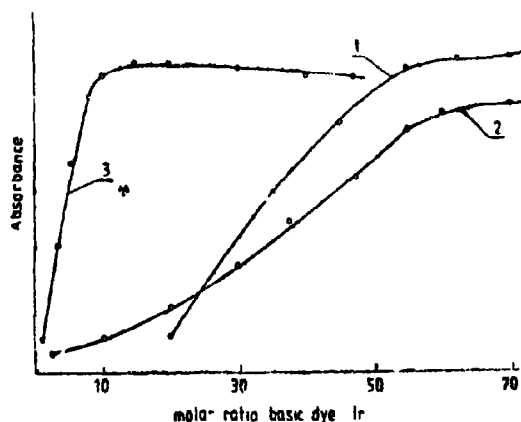
Fig. 1. Dependence of the formation of iridium ion associate on the molar excess of basic dye 1—rhodamine 6G, 2—malachite green, 3—crystal violet. Absorbances of the solutions measured against the blanks.

The ion pair of the $SnCl_3^-$ ion with rhodamine 6G separates together with the anionic iridium complex-basic dye associate. It is decomposed when the precipitate is washed with 2.5 *M* HCl. The excess of the dye can be removed nearly completely by shaking the precipitate and the di-isopropyl ether with 3 portions of 2.5 *M* HCl. The floated ion associates of iridium with malachite green and crystal violet are less stable than the ion associate with rhodamine 6G. Washing the precipitates with solutions of similar acidity as that used during floatation leads to decomposition of the floated compounds. The isolated precipitates of iridium with MG and CV can be washed only by shaking with the floating solvents (di-isopropyl ether and benzene, respectively).

Dissolution of the separated and washed ion associates in acetone, methanol, ethanol and dimethylformamide (DMF) was examined. In the case of the system with rhodamine 6G the precipitate dissolves in the latter three solvents after a little shaking The dissolution in acetone is immediate. The absorption spectra of the ion associate in these solvents differ insignificantly from the spectrum of the dye in water, with respect to the position of λ_{max}. The absorbance of the acetone solution does not change for a long time.

The ion associate with malachite green dissolves in DMF very slowly and in acetone after a little shaking. Dissolution in methanol and ethanol is immediate. The colour of these solutions does not change for several hours in darkness.

The ion associate with crystal violet dissolves readily in all solvents examined. It should be mentioned that in some preparations of DMF (presumably containing admixtures of reducing agents), the colour intensity of the dye decreases. The solutions of the crystal violet associate in various solvents exhibit small differences in the position of λ_{max} The stability of the absorbance of solutions depends on the intensity and nature of the incident light.

Composition of the floated compounds :

The molar ratios of iridium to dye in the isolated and washed compounds were determined with the aid of the logarithmic method of Bent and French[8] (Fig 2). The data obtained indicate the molar ratio of iridium to crystal violet as 1 : 1, to malachite green as 1 . 3, and to rhodamine 6G as 1 · 4. These results were confirmed by absorbance
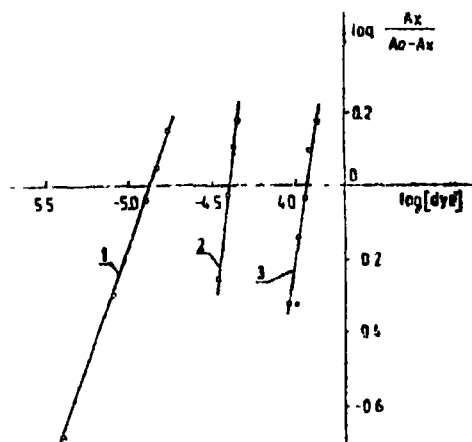
Fig 2 Determination of the molar ratios Ir . basic dye in the floated compounds by the Bent and French method : 1—crystal violet, 2—rhodamine 6G, 3—malachite green

measurements of the ion associate solutions containing known amounts of iridium, and of solutions of the dye salts (taken in suitable amounts) in solvents used.

In order to determine the number of tin atoms per one iridium atom in the washed compounds, they were mineralized and the tin in solutions

obtained was determined spectrophotometrically with phenylfluorone[9]. The ratios Ir : Sn calculated on the basis of the average result of several tin determinations were 1 : 5.2, 1 : 4.2, and 1 : 4.3 in the compounds of rhodamine 6G, malachite green and crystal violet, respectively. The postulated ratios of metals in the compounds are 1 : 5 or 1 : 4. The higher experimental results are undoubtedly due to contamination of the precipitates with tin not bound in the iridium compounds.

Bearing in mind that the oxidation state of iridium in presence of tin(II) is 3 and the coordination number of iridium is 6, the formulae of the floated compounds can be proposed.

The compound with rhodamine 6G can be postulated to be $[(R6G^+)_3IrCl_2(SnCl_3)_4^{3-}].[(R6G^+)(SnCl_3^-)]$. It follows from this formula that the compound is not a simple ion associate but an adduct of the iridium ion associate and of the $SnCl_3^-$ anion associate with dye. This adduct can be considered stable because it does not decompose during washing the precipitate.

The formula, $[MG^+]_3[IrCl_2(SnCl_3)_4^{3-}]$ can be proposed for the malachite green compound. In the floated compound with crystal violet the ratio of components Ir : Sn : CV is 1 : 4 : 1. In this case it is difficult to suggest a probable formula.

When the floatation of the ion associates with malachite green and crystal violet (triphenylmethane dyes) is carried out in light, the results show poor reproducibility. The lower results (absorbances of ion associates in polar solvents) are due to diminishing colour intensity of the pseudo solution prepared for flotation. The colour intensity decreases faster with higher concentration of tin(II). This effect is due to the photochemical reduction of malachite green and crystal violet to their inactive leuco forms. Light accelerates the reduction owing to polarization of electron structures of the dyes[10].

Flotation of the ion associates in the systems iridium(III)-tin(II)-chloride-R6G (MG or CV) can form a basis for sensitive flotation-spectrophotometric determination of iridium.

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A Simple Deviation Function to Summarize Data in Solvent Mixtures. The Standard Oxidation Potential of the Silver Chloride Electrode in Water-Ethylene Glycol Mixtures

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The data by Kundu *et al* on the standard oxidation potential of the silver chloride electrode in mixtures of water and ethylene glycol have been summarized using the simple deviation function introduced by the present writer. Over the whole range of concentration and temperature range studied the E° values (molality scale) can be fitted to within ±1 mV with six constants, of which two can be given theoretical meaning.

RECENTLY, a simple method to summarize thermodynamic data in solvent mixtures was devised[1]. In the paper the method is applied to some E°_m-data in water-ethylene glycol mixtures[2].

The model :

The basis is the zeroth approximation by Guggenheim[3]. According to this model the number of A-A pairs, B-B and A-B(=B-A) pairs in a mixture of the two components A and B, are given by x_A^2, x_B^2 and $2x_Ax_B$. Here x_A and x_B are the stoichiometric mole fractions of A and B in the mixtures.

It is now assumed that any property Y can be split into three parts, (y_A) which is a characteristic of solvent A, (y_B) characteristic of solvent B, and (y'_{AB}) characteristic of the mixtures. The following expression is thus obtained

$$Y=y_Ax_A^2+y_Bx_B^2+2y'_{AB}x_Ax_B \quad \cdot \quad (1)$$

This homogeneous equation is related to

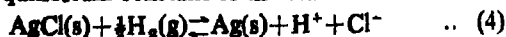
$$Y=y_Ax_A+y_Bx_B+y_{AB}x_Ax_B \quad \ldots (2)$$

by $$y'_{AB}=\tfrac{1}{2}(y_a+y_B+y_{AB}) \quad (3)$$

From plots of Y vs (x_A) or Y vs (x_B), the quantities y_A, y_B and y'_{AB} can be obtained using eqn (3). The use of these equations is illustrated below.

Application :

Instead of the E°_m-values use has been made of the equilibrium constant of the reaction

$$AgCl(s)+\tfrac{1}{2}H_2(g)\rightleftharpoons Ag(s)+H^++Cl^- \quad \ldots (4)$$

The equilibrium constant K_m is related to E°_m by

$$\log K_m=nFE^\circ_m/RT\ln 10 \quad \ldots (5)$$

Application of eqn (2) to reaction (4) gives

$$\log K_m=\log K_{EG}x+\log K_{H_2O}(1-x)+Bx(1-x) \quad (6)$$

x= the mole fraction of ethylene glycol (EG) in the mixture.

$\log K_{EG}=\log K$ of reaction (4) in pure ethylene glycol in molal units.

$\log K_{H_2O}=\log K$ of reaction (4) in pure water in molal units.

B= deviation function, which generally is assumed to be a function of x, most often expressed as a power series in x, i.e.

$$B=a+bx+cx^2+\ldots \quad \ldots (7)$$

At present only $B=0$ and $B=a$ can be given theoretical meaning. For $B=0$, y'_{AB} is the arithmetic average of Y in the two pure solvents. For $B=a$, y'_{AB} is constant and can be computed from eqn (3) provided y_A and y_B are constants. For B being a function of x, the approach is purely empirical, only offering a convenient way of summarizing experimental data.

The simplest way to approach a fitting of eqn (2) is to assume y_A and y_B to be correct and to evaluate B. In the present case it was thus found that eqn (7) could be reduced to

$$B=bx \quad \ldots (8)$$

i.e., only one empirical parameter. This implies that the data $\log K(x)$ can be fitted by a third degree polynomial

$$\log K=a_0+a_1x+a_2x^2+a_3x^3 \quad \ldots (9)$$

where $\log K_{H_2O}=a_0$

$$\log K_{EG}=\sum_0^3 a_i \text{ and} \quad \ldots (10a\text{-}c)$$

$$B=-(a_2+a_3)-a_3x$$

By using eqns (10a-c), the constants in eqn (9) can be transformed into the parameters in eqn (2). Values for $\log K$ at various concentrations computed from eqn (2) can then be transformed into E°_m-values using eqn (5).

Results and Discussion

In Table 1, experimental and computed E°_m-values are compared. The first column gives w, the weight per cent of EG in the mixture, then follows

Dedicated to Professor Arun K. Dey on his 60th birthday.

TABLE 1—EXPERIMENTAL AND COMPUTED E°_{m}-VALUES FOR THE SILVER CHLORIDE ELECTRODE IN WATER-ETHYLENE GLYCOL MIXTURES AT VARIOUS TEMPERATURES. DATA FROM REF 2. THE POTENTIALS ARE GIVEN IN MILLIVOLT

w	x	5° E°_{m}			15° E°_{m}			25° E°_{m}			35° E°_{m}			45° E°_{m}		
		exp	$b=5.30$	1 q	exp	$b=5\ 07$	1 q	exp	$b=4.64$	1 q	exp	$b=4.17$	1 q	exp	$b=3.91$	1 q
0	0	234 0	–	233 2	228 6	–	227.7	222.5	–	221.7	215.7	–	214.9	208.3	–	202.7
10	0.0312	226 7	228.4	227 6	221 2	222 8	222 1	215 1	216.4	215 9	208.2	209.6	209 0	200 9	202.0	201.6
30	0 1106	215 2	216 4	215 5	209 5	210 3	210.0	203.0	203.4	203.3	195 4	195.9	195 8	187.5	187.9	188.0
50	0 2249	202 8	203 2	202 6	196 5	196.4	196 1	189 6	188.4	188.8	181.0	179.8	180 3	172.3	171.0	171.5
70	0.4038	186 7	186.5	186 6	178 6	178.5	178.4	168.9	168.8	169 2	159 0	158.2	159.2	148.5	148 0	148.8
90	0 7232	141.5	140.4	141.6	129 8	130 5	130.1	118 3	118.3	118.3	106.4	105.2	106 4	93.7	93.1	93.6
100	1	4.60	–	46.0	34 9	–	34.8	23.5	–	23.5	11.8	–	11.8	−0.4	–	−0.3
		$\sigma(E^{\circ}_{m})$	±1.2	±0 5	$\sigma(E^{\circ}_{m})$	±1.0	±0 6	$\sigma(E^{\circ}_{m})$	±0.9	±0.6	$\sigma(E^{\circ}_{m})$	±1.2	±0.6	$\sigma(E^{\circ}_{m})$	±1.0	±0.6

TABLE 2—COEFFICIENTS IN THE POLYNOMIAL GIVEN BY EQN (9) TOGETHER WITH LOG K- AND B-EXPRESSIONS OBTAINED FROM Eqns (10a – c)

°C	$a_0 = -\log K_{H_2O}$	a_1	a_2	a_3	$\log K_{EG}$	B
5	4.226	−3.455	5 619	−5.557	0.833	$B = -0.06 + 5.56x$
15	3.983	−3 306	4.889	−4.957	0.609	$B = 0.07 + 4.96x$
25	3.747	−3 230	4 371	−4.495	0.397	$B = 0.12 + 4.50x$
35	3.515	−3.234	4.117	−4.206	0.193	$B = 0.09 + 4.21x$
45	3 290	−3 190	3.728	−3.833	−0.006	$B = 0.105 + 3.83x$

TABLE 3—COMPARISON OF EXPERIMENTAL E°_{m}-VALUES WITH THOSE COMPUTED FROM EQNS (12A – C). POTENTIALS ARE GIVEN IN MILLIVOLT

w	5° E°_{m}		15° E°_{m}		25° E°_{m}		35° E°_{m}		45° E°_{m}	
	exp	calcd	exp.	calcd	exp.	calcd.	exp.	calcd	exp	calcd.
0	234 0	234.6	228.6	228.2	222.5	221 8	215.7	215 4	208.3	209.0
10	226.7	229 0	221.2	222.4	215.1	215.8	208 2	209.3	200.9	202.7
30	215.2	217.0	209.5	209.9	203.0	202.8	195.4	195.7	187.5	188.6
50	202.8	203.9	196.5	195 8	189 6	187.8	181.0	179.7	172.3	171.7
70	186 7	187.4	178 6	177.7	168.9	168.0	159.0	158.3	148.5	148.6
90	141.5	141.4	129.8	129 4	118.3	117.5	106.4	105.6	93.7	93.6
100	46.0	46.3	34.9	34.8	23.5	23.2	11.8	11.6	−0.4	0
	$\sigma(E^{\circ}_{m})$	±1 4	$\sigma(E^{\circ}_{m})$	±0.7	$\sigma(E^{\circ}_{m})$	±1 0	$\sigma(E^{\circ}_{m})$	±0.8	$\sigma(E^{\circ}_{m})$	±1.0

the mole fraction of EG, $x_{EG}=x$. For each temperature three E°_{m}-values are given. First of these is the experimental value, then the value computed with B given by eqn(8), with the b-value given in the heading, and in the third column results of a least squares analysis using eqn (8). The parameters found by this method and the log$K$-values etc. computed using eqns (10a-c) are given in Table 2. Below the computed E°_{m}-values in Table 1 the standard deviation in E°_{m}, $\sigma(E^{\circ}_{m})$, is given,

$$\sigma(E^{\circ}_{m}) = \pm\sqrt{\Sigma(E^{\circ}_{m\ exp} - E^{\circ}_{m\ calcd})/(n-1)} \quad .. \ (11)$$

n=number of experimental points.

As can be seen from Table 1, the least squares fit with four constants gives a standard deviation of about ±0.5 mV, while the fit with one empirical constant roughly doubles the standard deviation to about ± 1.0 mV.

The log$K$-values in the two pure solvents as well as the constant b have been fitted to $1/T$ with least squares methods. The expressions arrived at are given below :

$$\log K_{H_2O} = -3.223 + 2079/T$$

$$\log K_{EG} = -5.833 + 1856/T \quad \ldots \ (12a\text{-}c)$$

$$b = -6.31 + 3250/T$$

A comparison between computed and experimental E°_{m}-values is made in Table 3.

As seen from Tables 1 and 3 the fit is about the same. A least squares fit to the constants given in Table 2 did not improve the fit and discarded in favour of eqns (12a-c).

It is evident from Tables 1 and 3 that with six constants (eqns 12a-c) it is possible to adequately fit the experimental E°_{m}-values both over the whole range of concentration as well as the temperature range investigated. Of the six constants obtained two have theoretical meaning, giving an estimate of ΔH for the reaction in question. The results presented here can be compared with the results of the authors

themselves, who fit E^{0}_{m} for each mixture studied with three constants in the expression

$$E^{0}_{m}=\sum_{0}^{2} a_{i}(t-25)^{i} \quad (t=\text{temperature in degree centigrade})$$

i.e. 21 constants instead of 6 only to fit the temperature dependence. The authors claim the fit to be about ±0.3 mV. However, to fit five experimental point with three constants leads to a large uncertainty in each constant. For that reason, the approach presented here does not only have the merit of giving a fair description of the concentration and temperature dependence of E^{0}_{m}, it also uses the minimum numbers of parameters to fit the deviations from additivity in the mixtures.

When comparing data from different authors on a certain system the agreement sometimes is rather poor. It is the intention of the present writer to use the approach outlined above to summarize data in the literature and try to give the most reasonable set of parameters, when comparing all available data on each system[4].

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Note added in proof : Since this paper was written the model has been extended to comprise the general case with B being a function of x (cf eqn 7) with all constants given a simple theoretical meaning. The application of this general approach to the data by Kundu *et al*[2] will be published elsewhere.

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Alkaloids of *Mitragyna parvifolia* (Roxb) Korth. and their Transformations

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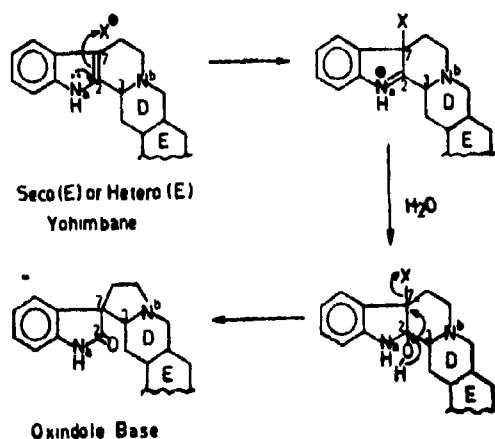
From the basic fractions of the leaves of *Mitragyna parvifolia* (Roxb) Korth. three oxindole alkaloids, mitraphylline, isomitraphylline and speciophylline N_b-oxide were isolated. A novel method has been developed for the transformation of mitraphylline, the major alkaloid of this species, to the corresponding heteroyohimbinoid base, ajmalicine without disturbing any chiral centre. Mitraphylline N_b-metholodide, when treated with triethyloxonium fluoroborate, was converted to its corresponding imino-ether which on reduction with sodium borohydride in acetic acid furnished ajmalicine N_b-metholodide. The latter could be transformed to ajmalicine by conventional procedure.

THE growing family of oxindole alkaloids has gained much importance on biogenetic grounds and also for the interesting chemical reactions displayed by them. These basic constituents originate from the alkaloids of secoyohimbane or heteroyohimbane series through the intermediacy of the corresponding indoleninium derivatives. The indoleninium intermediates on hydroxylation at the neighbouring carbon (C_2) (vide Chart 1) followed by the abstraction of the proton from the hydroxyl with the concomitant migration of C_2-C_8 bond at C_7 generate the oxindole derivatives. The key role in this transformation is played by the indolic nitrogen N_a. These alkaloids have been reported to occur in *Aspidosperma*, *Mitragyna*, *Ourouparia*, (*Uncaria*), *Rauwolfia* and *Vinca* species and bear a close structural resemblance to each other and possess the same basic framework (having C_2-C_8 bond cleavage) derived from tryptophan via its decarboxylation product tryptamine and secologanin, a C_{10}-unit of terpenoid origin.

Seco (E) or Hetero (E) Yohimbane

Oxindole Base

Chart—1

In recent years, intensive research is being pursued in this area and this has culminated in the isolation of many new oxindoles, several of these being stereomers having different configurations. Meaningful allocation of correct conformation of each configuration has been possible from spectral data (viz., pmr spectra) as spectral parameters are conformation-dependent.

The present communication is mainly concerned with the isolation of speciophylline N_b-oxide from *Mitragyna parvifolia* (Roxb) Korth. and the development of a new method for the conversion of mitraphylline, the major alkaloid of this species, to the corresponding heteroyohimbinoid base with the retention of chirality of the molecule. The genus *Mitragyna* is widely distributed in tropical and subtropical regions. Several *Mitragyna* species, which are large trees indigenous to South Eastern Asia, find commercial use in the timber and paper industries. The special feature of this genus is the ability to produce a large number of oxindole alkaloids having pentacyclic structures of ajmalicine type. *M. parvifolia* (Roxb) Korth. is a much investigated species and special mention may be made about the contribution of Shellard and his coworkers[1-8] towards systematic chemotaxonomic studies of this genus. From this particular plant occurrence of five alkaloids, viz., mitraphylline (1), pteropodine (2), isopteropodine (3), speciophylline (4) and uncarine F (5) (vide Chart 2) has been reported. It has been observed that environmental factor has a vital role to play in modifying the alkaloid content and the structure. It was therefore thought worthwhile to study the basic constituents of *M. parvifolia* which grows profusely in Bengal plain. The primary objective was to isolate mitraphylline (1), the major alkaloid of *M. parvifolia* and to evolve a new method for its conversion to pentacyclic heteroyohimbane system with the retention of configuration at the asymmetric centres as previously mentioned.

With this object, the leaves of this species were collected from the Indian Botanic Garden, Sibpur, West Bengal. The basic fractions of the alcoholic extract of the leaves yielded three oxindoles of which two were isomeric and already known

in the literature[4]. These were identified as mitraphylline (1) $C_{21}H_{24}N_2O_4$ (M^+368), m p. 265-7° and isomitraphylline (6) $C_{21}H_{24}N_2O_4$, m.p. 122-3° (vide Chart -), the oxindoles of normal series (D/E ring juncture being *trans*) having 15α H--20β H--19β H configuration. From the conformational analysis mitraphylline (1) was shown to be a stronger base than the other isomer (6). This is due to the proximity of the lactam carbonyl group to N_b which forms the ammonium ion on protonation. The protonated species has the unique advantage of undergoing stabilisation by H-bonding with the lactam carbonyl group This situation is not permitted in isomitraphylline. The third oxindole alkaloid was found to be an N_b-oxide of speciophylline (4) previously obtained from *Uncaria*[6] species only in trace amount. Thus the spectral investigations of the natural product were not possible which could only be studied with the synthetic one. In this communication we would like to report the physical properties of speciophylline N_b-oxide isolated from *M. parvifolia*. The compound was obtained in adequate quantity, thus permitting detailed studies of the molecule. It could be isolated as an amorphous solid, m.p. 113-5° from 10% methanolic chloroform eluates. The most significant feature of this base was its highly polar character and its resistance to migration on chromatoplates [R_f 0.65, developing system MeOH-Et_2NH (12 : 1)]. It showed characteristic oxindole colour reaction—spraying chromatoplate with a solution of 0.2 *M* $FeCl_3$ in 85% $HClO_4$ followed by heating the plates at 90° for 1 hr when a pink spot developed. Its mass spectrum showed a ready loss of 16 mass units generating the base peak at m/e 368 from the molecular ion peak at m/e 384. The remaining fragmentation pattern was practically the same as that of mitraphylline and isomitraphylline, the minor differences existing in relative peak intensities only. This observation clearly indicated that it is an N_b-oxide ($C_{21}H_{24}N_2O_5$) of the base having the composition $C_{21}H_{24}N_2O_4$.

Chart—2

The compound exhibited absorption maxima at λ_{max}^{EtOH} 220, 245 and 286 nm (log ε : 3.85, 4.01 and 3.23, respectively) similar to those of mitraphylline[4]. The ir spectrum also indicated its structural similarity with heteroyohimbinoid oxindole alkaloids excepting the appearance of an additional peak at 950 cm^{-1} owing to the presence of aliphatic N-oxide. The 90 MHz pmr spectrum of the compound studied in d_6-DMSO showed a three proton singlet at δ 3.20 attributed to the methyl group of the carbomethoxy function The C_{17}-*H* resonated as a singlet at δ 7.50 whereas C_{19}-*H* as a multiplet (J_1=6.5 Hz and J_2=1.5 Hz) at δ 4.35 with C_{19}-CH_3 as three proton doublet (J_1=6.5 Hz) at δ 1.22.

All these data indicate the compound to be an oxindole base with a heterocyclic ring E, stereoisomeric with mitraphylline. The exact position of $C_{19}-CH_3$ signal had been used to deduce the nature of D/E ring junction. Heteroyohimbine alkaloids with a *cis* D/E ring junction normally show doublets owing to C_{19}-CH_3 at δ 1.32-1.42 whereas those with *trans* D/E junction exhibit the corresponding signal at δ 1.16-1.19. It appeared that a similar criterion would also be valid in the ring E hetero-oxindole series, since the alkaloids with a *cis* D/E ring junction showed the doublets at δ 1.23-1.4 while those with a *trans* D/E junction showed the corresponding signal at δ 1.1-1.16 (the C_{19}-CH_3 of mitraphylline appearing at δ 1.16). The coupling constant values for C_{19}-*H* as observed in this case clearly indicated the α-orientation of C_{19}-CH_3 in either heterooxindole having *cis* or *trans* D/E ring junction. The four aromatic

protons in this alkaloid resonated as a multiplet around δ 6.84-7.30 indicating that the oxygen at N_b is on the opposite side of the molecule to C_9-*H*, otherwise the latter would have separately appeared downfield as a clear one proton double doublet. All these information revealed that the compound would be an N_b-oxide of either mitraphylline (1) or speciophylline (4). Mitraphylline (1) was converted to its N_b-oxide derivative on treatment with *m*-chloroperbenzoic acid and the product was found to be different from our alkaloid. Interestingly, the natural N_b-oxide of the base when reduced with H_2-Pd/C in ethanol and also with sulphurous acid was found to be identical with speciophylline (4). The identity of our alkaloid with speciophylline N_b-oxide was subsequently established by compa rison with an authentic sample

Since mitraphylline (1) could be isolated in appreciable quantity it was intended to develop a suitable method to convert it into the corresponding indole (tetrahydro β-carboline) derivative, ajmalicine (7), with the retention of chirality of the molecule. The method reported in the literature[5] for converting the oxindoles to the corresponding tetrahydro β-carboline derivative was to prepare the N_a-imino-ether from the oxindole with the strong electrophile $Et_3O^+.BF_4^-$ followed by reduction of the imino-ether with sodium borohydride in acetic acid to the corresponding indolic seco-compound When the cyclisation of ring C occurred the process ended up with C_3-epimers. Our objective was to generate the tetrahydro β-carboline derivative from the imino-ether with the retention of configuration at C_3.

To fulfil this requirement it was necessary to prevent participation of lone pair of electrons on N_b leading to the formation of seco-compound. Hence the basic nitrogen of mitraphylline was quaternised with CH_3I in dry THF, when mitraphylline N_b-methoiodide (8), $C_{22}H_{27}N_2O_4I$, d p. 260° separated out as a white solid in the reaction medium This quaternary salt was subsequently treated with dry methylene chloride solution of $Et_3O^+.BF_4^-$ under an oxygen free dry nitrogen blanket. The imino-ether derivative (9) thus obtained, was then subjected to reduction with sodium borohydride and glacial acetic acid to yield a single product $C_{22}H_{27}N_2O_3I$ (10), d.p. 235° The product showed ultraviolet absorption maxima at λ_{max}^{EtOH} 270 and 288 nm (log ϵ 3.9 and 3.75, respectively) similar to those of quaternary heteroyohimbinoid alkaloid[7]. The identity of the compound with ajmalicine N_b-methoiodide was finally established by comparing their co-tlc behaviour, ultraviolet absorption characteristics and superimposable infrared spectra. The methiodide was converted to ajmalicine (7), $C_{21}H_{24}N_2O_3$ (M^+ 352), m.p. 256°, uv λ_{max}^{EtOH} 226, 282 and 290 nm (log ϵ 4.64, 3.96 and 3.88, respectively) following the procedure of Karrer[7]. The identity of the base was established by comparison with authentic ajmalicine following the conventional procedure. The sequence of the aforesaid reactions is displayed in Chart 3.

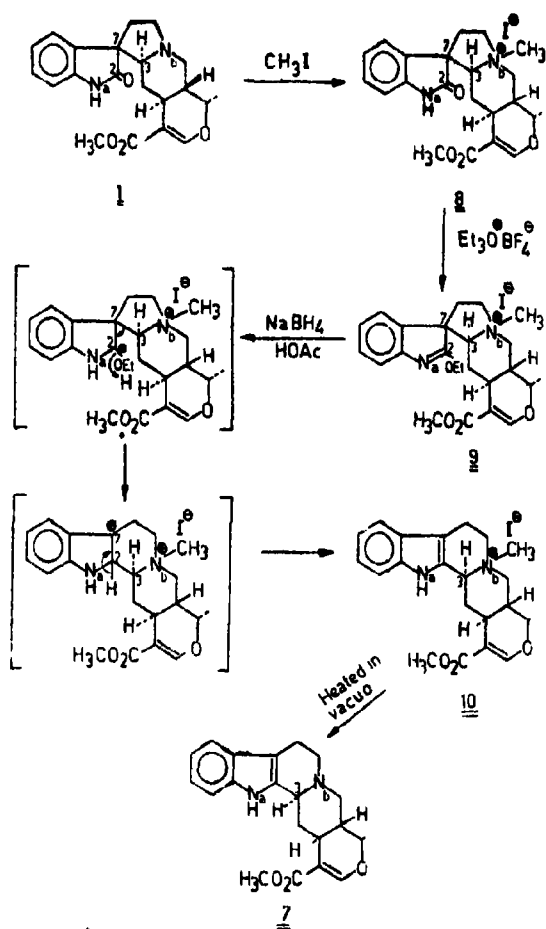



Chart - 3

Experimental

The melting points were determined in a Kofler block and are uncorrected The ultraviolet absorption spectra were recorded in a Carl-Zeiss VSU-1 Universal spectrophotometer in 95% aldehyde free ethanol and the infrared spectra in a Beckmann IR-20 spectrophotometer in KBr disc. The nmr spectra were recorded in a 90 MHz Brücker Spectrospin machine The solvents were dried over anhydrous sodium sulphate Column chromatography was carried out with Brockmann alumina and thin layer chromatography with silica gel G. The spots on the chromatoplates were detected by spraying Dragendorff's reagent.

Isolation of mitraphylline, isomitraphylline and speciophylline N_b-oxide: Finely pulverised dry leaves (10 Kg) of *Mitragyna parvifolia* (Roxb) Korth. were extracted with ethanol for three weeks. The ethanolic extract was then concentrated and churned with 5% aqueous citric acid for 72 hr. The neutral portion was separated and filtered off. The filtrate was basified with liquor ammonia in an ice-cold condition. The liberated base was taken up in chloroform, washed with water and dried. The chloroform concentrate was chromatographed over

:kmann alumina and the column was eluted with ents of increasing polarities.

The benzene-chloroform (3 : 1) and the chloro- ı eluates yielded mitraphylline, $C_{21}H_{24}N_2O_4$ + 368), m p. 265-7°, and isomitraphylline, $H_{24}N_2O_4$ (M^+ 368), m p. 122-3°, respectivcy n the 10% methanolic chloroform eluates speci- ylline N_b-oxide, $C_{21}H_{24}N_2O_5$ (M^+ 384), m p. 5° separated and crystallised as white flakes ı the same solvent mixtures. UV : λ_{max}^{EtOH} 220, 245 286 nm (log ε 3.85, 4.01 and 3.23, respectively). ν_{max}^{KBr} 3400, 1710, 1610, 950 cm^{-1} PMR in d_6-SO : δ 1.22 (3H, d, J_1=6.5 Hz, C_{19}-CH_3), 3.20 , s, -CO_2CH_3), 4.35 (1H, dm, J_1=6.5 Hz and 1.5 Hz, C_{19}-*H*), 6.87-7 30 (4H, m, aromatic ons), 7 50 (1H, s, C_{17}-*H*). MS: m/e 384 (M^+), (M-16), 223, 222, 208, 159, 146, 145, 144, 130 69.

Preparation of mitraphylline N_b-oxide : To a solu- of mitraphylline (10 mg) in dry chloroform was :d a solution of *m*-chloroperbenzoic acid in the : solvent. The temperature of the reaction ure was maintained at 0° for 3 hr. The result- nitraphylline N_b-oxide was isolated by prepara- tlc.

Reduction of speciophylline N_b-oxide : a) The ral N_b-oxide (2 mg) was dissolved in spectral hol and hydrogenated over Pd/C for 2 hr. The tion product on filtration and subsequent oval of the solvent furnished the parent oxindole iophylline, confirmed by co-tlc with an entic sample. b) The natural N_b-oxide (2 mg) treated with 5% sulphurous acid and the mixture allowed to stand for 1 hr. The tertiary base extracted with chloroform after the solution was : alkaline with ammonia, washed and dried. chloroform was removed and the residue was d to be identical with an authentic sample of iophylline.

Preparation of mitraphylline N_b-methoiodide : To lution of mitraphylline (100 mg) in dry THF ml) methyl iodide (10 ml) was added and reaction was stirred for 4 hr and kept over- t in the dark. Mitraphylline N_b-methoiodide, $H_{27}N_2O_4I$, d.p. 260°, separated out as white rphous solid (90 mg). Found : C, 51.65 ; H, ; N, 5.40. $C_{22}H_{27}N_2O_4I$ requires C, 51 76 ; .29 ; N, 5.49%.

Preparation of imino-ether of mitraphylline N_b-oiodide : To a well-stirred solution of triethyl- iium fluoroborate (3.5 g) in dry methylene chlo- (25 ml) a solution of mitraphylline N_b-metho- le (90 mg) in the same solvent (25 ml) was added wise under a completely dry and oxygen free gen blanket, stirring being continued for 10 hr. The reaction mixture was neutralised with a saturated solution of sodium bicarbonate in ice-cold condition The methylene chloride layer was separated, washed and dried. Removal of the solvent yielded a gummy mass which on trituration with dry ether afforded the desired imino-ether of the methoiodide (60 mg), $C_{24}H_{31}N_2O_4I$, d.p. 215°. Found : C, 53.45 ; H, 5 70 , N, 5 25. $C_{24}H_{31}N_2O_4I$ requires C, 53.53 ; H, 5 76 ; N, 5 20%

Reduction of the imino-ether of mitraphylline N_b-methoiodide to ajmalicine N_b-methoiodide : The above imino-ether (60 mg) was dissolved in glacial acetic acid and sodium borohydride (500 mg) was added portionwise to the solution, kept at a low temperature. After the effervescence ceased, the mixture was allowed to stand at room temperature for 10 hr and later basified with liquor ammonia. The liberated base was taken up in chloroform (3×30 ml), washed and dried On removal of the solvent a gummy residue was obtained. On trituration with dry ether the residue solidified (20 mg), $C_{22}H_{27}N_2O_3I$, d.p 235° UV λ_{max}^{EtOH} · 270 and 288 nm (log ε 3 9 and 3.75, respectively). Found · C, 53.35 , H, 5 53 , N, 5 75 $C_{22}H_{27}N_2O_3I$ requires C, 53 44 ; H, 5 46 , N, 5.66%.

Conversion of ajmalicine N_b-methoiodide to ajmalicine : Ajmalicine N_b-methoiodide obtained above was heated in a sealed tube under vacuum at 220-25° for 10 min The residue was taken up in chloroform Ajmalicine (yield 25%) crystallised from ether, $C_{21}H_{24}N_2O_3$ (M^+ 352), m.p. 252°. UV : λ_{max}^{EtOH} 226, 282 and 290 nm (log ε 4.64, 3.96 and 3.88, respectively) Its identity was established by comparison with an authentic sample by co-tlc, m.m.p. and superimposable ir spectra.

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Alkaloids of *Machilus glaucescens* Wight : Machigline, A New Phenolic Oxoaporphine Alkaloid

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Machigline (I), a new phenolic oxoaporphine alkaloid, isolated along with atheroline (II) and β-sitosterol-O-β-D-glucoside from the alcohol extract of the leaves of *Machilus glaucescens* Wight (Lauraceae), has been shown to be 1,2-methylenedioxy-9-hydroxy-10-methoxyoxoaporphine by spectral and chemical studies A fatty ketol characterised as a rarely occurring *n*-hentriacontan-10-ol-16-one (≡ 10-hydroxypalmitone) (III) (first report of its occurrence in Lauraceae) has also been isolated as an aliphatic constituent from the $CHCl_3$ extract of the plant besides the lignan and nor-lignan constituents The mass fragmentations of I and III have been delineated. The isolation of machigline and atheroline constitutes the first report on the occurrence of oxoaporphines in *Machilus* species, and machigline adds a new name to the list of only a few phenolic oxoaporphines

THE family Lauraceae is a well-known rich source of alkaloids and some *Machilus* species are reported to elaborate benzyltetrahydroisoquinoline and aporphine alkaloids[1-3] Earlier, we reported[4] the isolation, structure elucidation and synthesis of three new nor-lignans viz., machicendiol, machicenonol and machicenin from *Machilus glaucescens*. We now report the isolation of a new phenolic oxoaporphine alkaloid designated machigline[5] (I) along with atheroline (II)[6,7] and β-sitosterol-O-β-D-glucoside from the alcohol extract of the plant material and the isolation of a rarely occurring ketol 10-hydroxypalmitone[8] (III) from the $CHCl_3$ extract as the major aliphatic constituent of the plant.

The minor alkaloid machigline crystallising from chloroform-methanol as glistening red needles, m.p. 315° (d), $C_{18}H_{11}O_5N$ (M^+ 321.0620), $[\alpha]_D \pm 0°$, has been assigned structure (I) on the basis of spectral and chemical studies. Machigline is insoluble in common non-polar solvents but fairly soluble in alcohol and methanolic-chloroform and forms red solution with mineral acids The intensity and the variation of colour of machigline in solution from yellow to pink and to red depend on the concentration and the *p*H of the medium. This behaviour is reminiscent of phenolic oxoaporphine alkaloids[6,7] The presence of the phenolic hydroxyl

(I), R = H
(IV), R = $COCH_3$
(V), R = CH_3

(II), R = H
(VI), R = $COCH_3$

$CH_3(CH_2)_8-CH(OH)-(CH_2)_4-CH_2(b)-C(R)(R^1)-CH_2(a)-(CH_2)_{13}-CH_3$ (C-10, C-16)

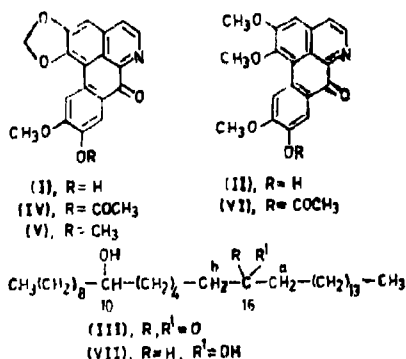
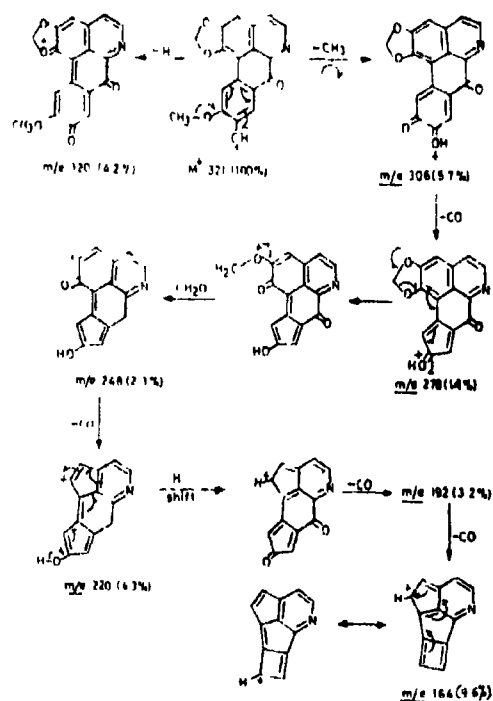
(III), R,R[1] = O
(VII), R = H, R[1] = OH

group is also suggested by positive $FeCl_3$ colouration. Its solubility in Na_2CO_3 solution indicates its enhanced acidity compared to simple phenols. The oxygenation sites in the oxoaporphine skeleton as

TABLE 1—UV AND VISIBLE ABSORPTIONS OF MACHIGLINE AND ATHEROLINE

Compound	λ_{max} (EtOH)		λ_{max} (EtOH + HCl)		λ_{max} (EtOH + NaOH)	
	nm	log ε	nm	log ε	nm	log ε
Machigline	249	4.23	258	4.19	254	4.28
	272	4.12	281	4.10	304	4.26
	285	4.04	379	3.92	326	4.21
					351	3.79
	351	3.70	509	3.27	382	3.43
	385	3.22				
	430	3.18			537	3.28
Atheroline	244	4.12	257	4.10	252	4.12
	273	4.17	282	4.10	294	3.99
	292 (sh)	3.96	385	4.05	320	3.98
	355	3.90	500	3.38	390	3.74
	380	3.83			535	3.46
	435	3.60				

well as the location of the hydroxyl function was settled from a comparative study of its uv and visible spectra (Table 1) with those of the congener alkaloid atheroline[6] and other phenolic oxoaporphines[9]. Machigline displays a very characteristic 1,2-methylenedioxy phenolic oxoaporphine uv spectrum. It contains one methoxyl group (pmr and ms) and thus it appears to be a 1,2-methylenedioxy methoxy phenolic oxoaporphine. The close similarity of the uv and visible spectra of machigline and atheroline in different media and similar bathochromic shifts of λ_{max} values in alkali [phenolate anion from machigline is comparable in energy to that from atheroline] indicate the same location (C-9) for OH in both the alkaloids thus allowing delocalisation of the charge of the phenolate anion to nitrogen. Any other alternative position for phenolic OH group would have given rise to different uv maxima in alkali medium due to different mesomeric stabilisation of the phenolate ion[9]. In machigline, like atheroline, the greater mesomeric stabilisation of the phenolate ion accounts for its well-marked acidic properties compared to simple phenols. The ir spectrum (ν_{max}, cm^{-1}) of machigline exhibited characteristic bands for OH (3520), conjugated CO (1635) in the highly aromatic oxoaporphine system (1575, 1522) and methylenedioxy[10] (962) group

The pmr spectra of machigline and atheroline show close similarity in the aromatic region suggesting the same positions of oxygenation functions in them The pmr spectrum (80 MHz, d_6-DMSO) of machigline (Table 2) clearly shows a methylenedioxy grouping on the planar oxoaporphine ring system as a two proton singlet[11,12] at δ 6.48, an aromatic methoxyl at δ 3.96 (3H, *s*) and the five aromatic protons in δ 7.46-8.71 region and the hydroxyl proton at δ 9.9 (1H, *s*). The placement of methylenedioxy group is made by a comparative study of the pmr spectra of some methylenedioxy oxoaporphines in conjunction with the uv and mass spectral analysis. The chemical shifts of methylenedioxy and methoxyl protons in oxoaporphines vary with their locations. It is known that a methylenedioxy group located at 1,2 resonates at a lower field (δ 6.5-6.85) than if located at 9,10 (δ 6.2)[7,13,14] The presence of an aromatic singlet at δ 7.46 due to H-3 resonating at higher field than other aromatic protons eliminates the possibility of methoxyl group being at C-3 (moreover a C-3 methoxyl appears between δ 4 43-4.55 i.e., a comparatively lower field[9]). The two one proton doublets centred at δ 8 71 and 7 92 are assignable to H-5 (α to N) and H-4, respectively ($J_{4,5}=J_{5,4}=5$ Hz) of the pyridine moiety. The appearance of the remaining two aromatic protons as two singlets indicates the adjacent positions of hydroxyl and methoxyl groups at C-9 and C-10 or vice-versa. The singlet at δ 8.03 is due to H-11 which in oxoaporphines appears more downfield[9] than H-3, H-8, H-9 or H-10 and that at δ 7.66 is assigned to H-8 (adjacent to 9-OH) appearing at the same field in both machigline and atheroline.

SCHEME 1 MASS FRAGMENTATION OF MACHIGLINE

The conversion of machigline to dicentrinone[15,16] (IV) ($\equiv$1,2-methylenedioxy-9,10-dimethoxyoxoaporphine) by treatment with excess CH_2N_2 in methanolic solution confirms the skeleton and the oxygenation sites at 1,2,9 and 10 positions. The location of the hydroxyl group at C-9 has been

TABLE 2—CHEMICAL SHIFT (δ) OF PMR SIGNALS OF MACHIGLINE, ATHEROLINE AND THEIR ACETATES (VARIAN CFT-20, 80 MHz)

Compounds (Solvent)	-O-CH₂-O	Aromatic protons H-3	H-4	H-5	H-8	H-11	C_9-O*H*	OC*H*₃ (1,2)	C_{10}-OCH₃	C_9-O-CO-C*H*₃
Machigline (d_6-DMSO)	6.48	7.46	7.92	8 71	7 66	8.03	9 9	—	3 96	—
Machigline acetate ($CDCl_3$)	6.48	7.12	7.65	8.82	7.99	8.16	—	—	3.95	2.02
Atheroline (d_6-DMSO)	—	7.46	7.91	8.69	7.67	8.56	9.91	3.95, 3.98	3.95	—
Atheroline acetate ($CDCl_3$)	—	7.12	7.67	8.81	8.00	8.70	—	3.96, 4.02	4.02	2.2

conclusively settled by observing the 0.33 and 0.13 ppm downfield shifts of H-8 and H-11 respectively (*ortho* and *meta* to acetoxy group) in machigline acetate, m.p. 240° (d) compared to machigline itself which are the same as those in atheroline acetate relative to atheroline. The mass fragmentation[17] (Scheme 1) pattern of machigline is in good agreement with the proposed structure (I). The spectrum shows loss of one methyl from the molecular ion (M^+ 321 0620) peak and the other ion peaks originated through the loss of CH_2O and a number of CO units. Thus, on the basis of the spectral studies in conjunction with the chemical observations, machigline is correctly formulated as (I). Moreover, there is report of natural occurrence of oxoaporphines bearing hydroxyl function at 9- but not at 10-position e.g., atheroline, subsessiline[18] and oxoanolobine[19]. The known congener alkaloid atheroline was isolated as a major constituent as a dirty yellow solid, $C_{19}H_{15}O_5N$ (M^+ 337), m.p. 248-50° (d) and its identity was established by comparison with an authentic sample. It is worthwhile recording the pmr spectrum of atheroline itself (Table 2) as it has not been reported earlier.

The major aliphatic constituent $C_{31}H_{62}O_2$ (M^+ 466 4660), m.p. 96°, isolated from chloroform extract was characterised as 10-hydroxypalmitone (III) which was first isolated from sandal leaves[8]. This fatty ketol [ir peaks at 1705, 3300 (br) cm^{-1}] afforded an acetate, m p. 43°. No spectral details of this compound and its $NaBH_4$ reduction product (VII) (which is not naturally or synthetically known) are available in literature and these are also reported in the present paper The compound (III) showed pmr signals ($CDCl_3$, TMS) at δ 3.6 (1H, *m*, -C*H*OH), 2 39 [*t*, J=7 Hz, 4 H, two CH_2 (*a* and *b*)], 1 27 [*b s*, 50 H, $(CH_2)_{25}$] and 0.89 [*t*, J=6 Hz, 6 H, two CH_3 groups]. The mass spectral analysis (Scheme 2) is quite interesting and is helpful to find the positions of carbonyl and hydroxyl groups. $NaBH_4$ reduction of the ketonic alcohol yielded the straight chain diol, $C_{31}H_{64}O_2$ (M^+ 468), *n*-hentriacontan-10,16-diol (VII) showing pmr signals at

Scheme—2 Mass fragmentation of *n*-hentriacontan-10-ol-16-one

δ 3.55 [2H, *m*, two -C*H*OH], 1.26 [*b s*, 54 H, $(CH_2)_{27}$] and 0.86 [*t*, J=6 Hz, 6 H, two CH_3]. The absence of any triplet around δ 2.39 for ketomethylenes as in III as well as the absence of any carbonyl band in the ir spectrum of VII confirms the complete conversion of III into the diol (VII). The mass spectrum of the diol (VII) showed ion peaks at *m/e* 450 ($M^+ - H_2O$), 432 (m/e 450$-H_2O$ indicating the presence of two hydroxyl groups and appearance of a number of other peaks due to subsequent loss of methylenes. The isolation of atheroline and machigline marks the first occurrence of oxoaporphines in a *Machilus* species and machigline adds a new name to the list of only a few natural phenolic oxoaporphines

Experimental

Melting points were determined in H_2SO_4 bath and are uncorrected. The uv spectra were recorded on a Varion Techtron series 634 spectrophotometer in aldehyde free 95% ethanol. IR spectra were taken in KBr pellets with Beckmann IR-20 or Pye Unicam SP 1025 spectrometer and the optical rotations were measured on a Perkin-Elmer 241 polarimeter in $CHCl_3$ and ethanol solutions. PMR spectra of the original alkaloids were determined in d_6-DMSO and those of the acetates of the alkaloids and other compounds in $CDCl_3$ using TMS as internal standard with a Varian CFT-20 spectrometer. Silica gel (60-120 mesh) was used for chromatography of main columns and silica gel (100-200 mesh) for side columns. Anhydrous Na_2SO_4 was used for drying organic solvents. R_f values were measured over tlc on silica gel G.

Extraction : The marc left after pet. ether and $CHCl_3$ extraction of the dried and powdered leaves of *Machilus glaucescens* was kept immersed in EtOH (90%) for 20 days. The gummy brown residue (15 g) obtained from the alcohol extract responded to Dragendorff test for alkaloids. A small part of the residue (4 g) was repeatedly extracted with cold 2*N* HCl (4×100 ml) till the fresh extract showed negative test for alkaloid. The combined acid extract (400 ml) was cooled, basified with 2*N* NH_4OH solution and extracted with $CHCl_3$ (3×150 ml). The combined $CHCl_3$ extract (450 ml) was washed, dried and concentrated under reduced pressure. The deep brown gummy residue (residue-A) was found to be completely soluble in aqueous Na_2CO_3 or NaOH solution showing the presence of phenolic base. The original residue was also found to be almost soluble in Na_2CO_3 solution and negligible precipitation occurred on acidification of the alkali solution. The crude base was almost soluble in both acid and alkali. As the crude base was found to be weakly acidic (phenolic base), the direct chromatography of the crude extract was done over silica gel which effected better result without much loss compared to the case of usual acid extraction. Chromatography of the alcohol extract resulted in isolation of an uncharacterised fatty alcohol (250 mg), m.p. 80°, ν_{max} 3490 cm^{-1}, from the pet. ether-benzene (1 : 1) eluates and β-sitosterol (200 mg), m p 138° from the benzene fractions. The brown residue obtained from the $CHCl_3$-MeOH (95 : 5) eluates showed three spots of which two were very close on tlc [R_f 0.35, 0.5, 0.53, silica gel G, $CHCl_3$-MeOH (90 : 10)]. The last two spots were yellow coloured (concave shaped) and turned pinkish yellow after staining with iodine (phenolic). They showed bright pinkish red uv fluorescence. On repeated chromatography, the $CHCl_3$-MeOH eluates on concentration showed a white amorphous solid to float on the surface of the deep wine red coloured solution. The white solid on repeated crystallisations from $CHCl_3$-MeOH-CH_3COCH_3 mixture afforded β-sitosterol-O-β-D-glucoside, m.p. 265-70°d, ν_{max} 3420 (br OH), 2940, 1460, 1372, 1155, 1065 and 1020 cm^{-1}, acetate (Py/Ac_2O, 40 hr, r t.) m.p 168°, $[\alpha]_D$ $-27°$ (*c*, 1.77, $CHCl_3$), ν_{max} 1740 and 1220 cm^{-1}. Hydrolysis of β-sitosterol-O-β-D-glucoside in 10% H_2SO_4 in aqueous MeOH (reflux 1hr) afforded β-sitosterol after usual work-up and the aqueous sugar part was found to contain D-glucose identified by paper chromatography with authentic sample.

Isolation of atheroline : After separation of β-sitosterol-O-β-D-glucoside, the wine red coloured filtrate was concentrated and found to have two yellow coloured spots, R_f 0.50, 0.53 of varying intensity, similar to those of residue-A obtained by acid extraction of the alcohol extract. The mixed brown residue (1.0 g) was then chromatographed over silica gel (100-200 mesh) but as the R_f values of both the components (phenolic alkaloids) were close, separation by chromatography alone was not possible. Repeated careful fractional crystallisations from $CHCl_3$-MeOH-ether mixture and chromatography of the mother liquors followed by fractional crystallisations ultimately effected their separation. The major snuff coloured alkaloid (25 mg) was subsequently identified to be atheroline (comparison with an authentic sample obtained through the courtesy of Prof M P Cava), m p. 248-50°d, R_f 0.54 [silica gel G, $CHCl_3$-MeOH (90 : 10)], ν_{max} 3270, 1635, 1565, 1505, 1450, 1425, 1350, 1270, 1242, 1220, 1138, 1054 and 1000 cm^{-1}; acetate (Py/Ac_2O, 48 hr, r.t.), m p 190°d, crystallised from $CHCl_3$-pet. ether as yellow needles, ν_{max} 1745, 1640, 1585, 1495, 1450, 1340, 1205, 1110 and 1010 cm^{-1}.

Attempted catalytic hydrogenation of atheroline : Atheroline (8 mg) in AcOH was hydrogenated at r t. for 2 hr using PtO_2 as catalyst (2 moles of H_2 consumed) to a pale yellow solution which turned reddish brown on exposure to air for work-up. The residue after usual work-up and chromatographic purification was found to be identical with atheroline, m.p. 230°d

Action of $NaBH_4$ on atheroline : Atheroline (8 mg) in dry MeOH (8 ml) was treated with excess $NaBH_4$ (40 mg) and kept for 48 hr. After usual work-up, the resulting yellowish brown mass on chromatography afforded atheroline (5 mg), m.p. 240°d.

Isolation of machigline : After removal of atheroline by repeated chromatography and crystallisations, the mother liquors were mixed and

concentrated. The residue was chromatographed over neutral alumina (B.D.H.). The $CHCl_3$-MeOH (80 : 20) eluates on evaporation yielded machigline in poor yield (20 mg) crystallising from MeOH as glistening red needles, R_f 0.5 [$CHCl_3$-MeOH (90 : 10)], m.p. 315°d, bright pink fluorescence in uv light, ν_{max} 3520, 1635, 1575, 1522, 1465, 1426, 1355, 1280, 1212, 1140, 1092, 1055, 965 and 863 cm^{-1}.

Preparation of machigline acetate: Machigline (6 mg) was treated with pyridine (3 drops) and Ac_2O (1 ml) and warmed for 10 min on water bath and then kept for 48 hr. After usual work-up, machigline acetate was obtained as red needles, m.p. 230°d from $CHCl_3$-petrol mixture. ν_{max} 1730, 1640, 1575, 1522, 1460, 1250 and 962 cm^{-1}.

Conversion of machigline to dicentrinone: A methanolic solution (3 ml) of machigline (5 mg) was added to an excess of ethereal diazomethane solution when a yellow solid settled down due to its insolubility in ether. It was then kept with excess of the reagent at r.t for 3 days. The yellow solid obtained after removal of ether was found to be a mixture of dicentrinone (identified by comparison of spectra of authentic dicentrinone obtained from Prof M. P. Cava) and unreacted machigline, which was separated by chromatography. Dicentrinone (M^+ 335) had m.p. 300°d, crystallised from $CHCl_3$-MeOH solution, ν_{max} 1640, 1052 and 962 cm^{-1}.

Isolation of 10-hydroxypalmitone from $CHCl_3$ extract: Separation of lignan constituents of *M. glaucescens* has been described in an earlier communication Analysis of its aliphatic constituents resulted in the isolation of 10-hydroxypalmitone from $CHCl_3$ and $CHCl_3$-MeOH (98 : 2) eluates of the main chromatogram, crystallised from pet. ether and $CHCl_3$ mixture as globules and from $CHCl_3$-MeOH mixture as flakes, m p. 96°, $[\alpha]_D \pm 0°$ ($CHCl_3$). ν_{max} 3320, 2930, 2870 and 1706 cm^{-1}, acetate, m p 43° (pet.ether-benzene), ν_{max} 1720 and 1240 cm^{-1}.

$NaBH_4$ reduction of 10-hydroxypalmitone to n-hentriacontan-10,16-diol: 10-Hydroxypalmitone (15 mg) was added to an excess of $NaBH_4$ in MeOH solution and was kept at r.t for 40 hr. The diol (VII), m.p. 99°, was isolated after usual work-up and crystallisation from $CHCl_3$-MeOH mixture, $[\alpha]_D \pm 0°$ ($CHCl_3$), ν_{max} 3300 cm^{-1}, m/e (%) 450 (M^+—H_2O, 4.5), 432 (m/e 450—H_2O, 11.2), 323 (20.9), 309 (32.2), 305 (13.9), 291 (1?.1), 257 (8 8), 241 (40.6), 239 (83.5), 221 (47.5), 210 (17.7), 208 (13 6), 194 (8.8), 171 (21.8), 157 (15.5), 137 (20 7), 125 (23 7), 111 (39.9), 83 (100.0) and 57 (83.5)

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Structure and Synthesis of Mukoline and Mukolidine, Two New Carbazole Alkaloids from *Murraya koenigii* Spreng.

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and

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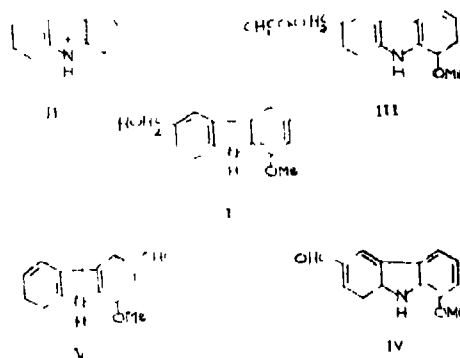
Mukoline and mukolidine, two new carbazole alkaloids from *Murraya koenigii* **Spreng, have been assigned the structures 6-hydroxy-methyl-1-methoxy carbazole and 6-formyl-1-methoxy carbazole, respectively**

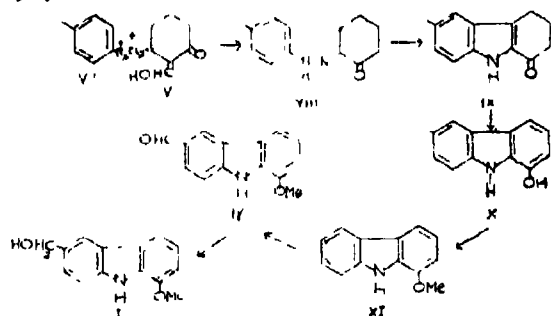
IN continuation of our interest in the carbazole alkaloids of the genus Murraya[1], we now report two minor alkaloids of C-13 skeleton isolated from the benzene extract of the roots of *Murraya koenigii* Spreng. The first compound, $C_{14}H_{13}NO_2$ mukoline (I), m p. 115-20°, was optically inactive and gave a red picrate, m p 230°. The uv spectrum of I [λ_{max}^{EtOH} 221 (4 60), 242 (4.85), 252 (4 65), 258 (4.0), 280 (3.4), 290 (3.6), 320 (3.0) nm] suggested the presence of a 1-methoxy carbazole chromophore in it. The ir spectrum showed the presence of a hydroxyl group, NH-function and aromatic residue [ν_{max}^{Nujol} 3440, 3240, 1610 cm^{-1}]. The nmr spectrum of mukoline (in $CDCl_3$) indicated the presence of NH-function (δ 8.22), aromatic protons (δ 7.0-7.9), deshielded benzylic methylene protons (δ 4.75), a hydroxyl proton (δ 4.45), aromatic methoxy protons (δ 3.9) and the meta-coupled aromatic proton at C-5 (J=2 cps).

The mass spectrum of I showed a molecular ion peak at m/e 227 and other significant peaks were at m/e 212 (M-15), 196 (M-31), 154 (M-15-31-28). The peak at m/e 154 could be represented by the ionic species (II) previously reported from glycozoline[2] and mukonine[3].

Mukoline (I) on methylation with K_2CO_3 in acetone furnished the N-methyl derivative $C_{15}H_{15}NO_2$, m p. 140° the uv spectrum of which was very similar to that of 1-methoxy carbazole. On acetylation, mukoline (I) gave an *o*-acetate (III) $C_{16}H_{17}NO_3$, m.p. 145° [M$^+$ 269] ν_{max} 1720 cm^{-1}. The uv spectrum of the acetate was similar to that of I showing that the hydroxyl group was in the side chain. These data together with the nmr spectral data of I were suggestive of the presence of a CH_2OH group on carbazole nucleus which was confirmed by oxidation of I to its formyl derivative (IV), $C_{14}H_{11}NO_2$, m.p. 152-55°, ν_{max} 1660 cm^{-1}, [M$^+$ 225]. The uv spectrum of (IV) [λ_{max} 238 (4.74), 248 (4.46), 275 (4 82), 290 (4.48), 330 (4.34)] was very similar to that of 3-formyl carbazole but not super-imposable with murrayanine[4] (V). It (IV) was also not identical with murrayanine (V) [m.p., m.m p, tlc]. The aldehyde (IV) on decarbonylation furnished 1-methoxy carbazole [λ_{max} 241 (4.5), 286 (3 84), 320 (3 46)] confirming that IV is 1-methoxy-6-formyl carbazole Therefore, mukoline could be formulated as 1-methoxy-6-hydroxy methyl carbazole This was also substantiated by comparison of I with 1-methoxy-3-hydroxy methyl carbazole[4], previously obtained by Na-borohydride reduction of murrayanine (V), when it was found that these two compounds were nonidentical.

Along with mukoline, another homogeneous, optically inactive carbazole alkaloid $C_{14}H_{11}NO_2$, m p. 152-55°, [M$^+$ 225] was obtained from the same plant. The compound, named mukolidine (IV), gave a 2,4-DNPH derivative. The ir spectrum of mukolidine showed the presence of a NH-function (3185 cm^{-1}), aldehyde function (1660 cm^{-1}) in an aromatic system. The uv spectrum of IV [λ_{max} 238, (4.74), 248 (4 46), 275 (4 82), 290 (4 48), 330 (4.34)], was very similar to that of a 3-formyl carbazole.

* Dedicated to Professor A. K. Dey on the occasion of his 60th birth day anniversary. Part 50 in Chemical (Molecular) Taxonomy.

The nmr data of IV showed the presence of an aldehyde proton (δ 10.8, s, 1H), -NH- proton (δ 8.6, s, 1H), aromatic protons (δ 8.15, 8.08, 7.3-7.6) and an aromatic methoxy group (δ 4.05, s, 3H). The nmr data together with the mass spectral fragmentation [m/e 225, 210, 182, 167] showed it to be a 3 or 6 formyl carbazole with methoxy group in it. The position of the methoxyl, group was determined by decarbonylation of IV when 1-methoxy carbazole was obtained. On borohydride reduction mukolidine (IV) furnished an alcohol identical with mukoline (I) (m.m.p., ir, uv). So, it appeared that mukolidine was 1-methoxy-6-formyl carbazole and was identified with the oxidation product of mukoline as detailed above (m.m.p., ir, uv). The conclusions were supported by synthesis below.

2-Hydroxy methylene cyclohexanone (VI) was reacted with toluene diazonium chloride (VII) under Japp-Klingemann conditions when 1,2-dione-1′-(4′-methyl) phenyl hydrazone (VIII), m.p. 205° was obtained. The hydrazone (VIII) on indolization with a mixture of acetic acid and hydrochloric acid furnished 6-methyl-1-oxo-1,2,3,4-tetrahydro carbazole (IX), m.p 190° which on dehydrogenation with Pd/C at 180° gave a 6-methyl-1-hydroxy carbazole (X) On methylation with diazomethane, the hydroxy compound (X) gave a crystalline homogeneous methoxyderivative (XI), m.p. 150°. On oxidation with DDQ, the compound (XI) gave an aldehyde which was found to be identical with mukolidine (IV) by direct comparison. The synthetic mukolidine on reduction with sodium borohydride furnished the hydroxymethyl derivative, m.p 115-20° which was found identical with mukoline (I) Thus the structures of (I) and (IV) were confirmed by synthesis

The oxidative functional variants of C-methyl group at 3-position[5] i.e., CHO, COOH, COOMe have been encountered in carbazole alkaloids. Mukoline provides the first example of the occurrence of hydroxymethyl group, an oxidative variant of CH_3 at 6-position of carbazole alkaloids. The hydroxymethyl group of mukoline (I) has been oxidised to CHO group in mukolidine (IV).

Experimental

All melting points are uncorrected. Petroleum ether used had the b p. 60-80° unless otherwise mentioned. The alumina for column chromatography and the silica gel for thin layer chromatography were supplied by Sarabhai Chemicals of India.

Isolation of mukoline (I) *and mukolidine* (IV). Air dried finely powdered roots of *Murraya koenigii* Spreng. (1Kg) was soxhleted for 48 hr with benzene. The extract was concentrated and chromatographed over alumina. The petroleum ether extract on evaporation gave a solid residue which on recrystallisation from benzene yielded mukolidine, m p 152-55°. [Found: C, 74. ; H, 4.55, N, 6 06 ; O, 14 4. $C_{14}H_{11}NO_2$ requires C, 74.6 ; H, 4 8, N, 6 2 ; O, 14.2%]. It gave a 2,4-DNPH derivative melting at 300°.

The benzene, benzene-chloroform eluents from the same chromatographic column on evaporation gave an oily residue which on recrystallisation from a mixture of benzene and petroleum ether furnished homogeneous crystals of mukoline, m.p. 115-20° which on recrystallisation melted at 118°. [Found C, 73.85 ; H, 5.70 ; N, 6.15 ; $C_{14}H_{13}NO_2$ requires C, 74.0 ; H, 5.72 ; N, 6.16%] It gave a picrate which on crystallisation from benzene melted at 230°.

N-methyl mukoline : A mixture of mukoline (25 mg) in dry acetone (12.5 ml), methyl iodide (0.5 ml) and potassium carbonate (250 mg) was refluxed for 6 hr. It was then filtered. On working up, the filtrate furnished crystals which after filtration and recrystallisation from benzene-pet. ether mixture gave a homogeneous compound, m.p. 140° [Found: C, 74 5 ; H, 6.1 ; N, 5.6. $C_{15}H_{15}NO_2$ requires C, 74 6 ; H, 6.2 ; N, 5.7%].

Acetylation of mukoline : Mukoline (10 mg) in acetic anhydride (0.1 ml) was heated with sodium acetate on water bath for 6 hr. The reaction product on working up furnished crystals which on recrystallisation from benzene-pet. ether mixture melted at 145°. [Found : C, 78.65 ; H, 5.46 ; N, 5.15 $C_{18}H_{17}NO_4$ requires C, 78.80 ; H, 5.57 : N,5.20%]

Oxidation of mukoline with active MnO_2 : *Formation of the formyl derivative* (IV) : To a solution of mukoline (50 mg) in dry CCl_4 (30 ml), active MnO_2 (500 mg) was added. The mixture was stirred for 5 hr and filtered. The filtrate after removal of the solvent yielded a solid, m.p. 152-55° which on sublimation and recrystallisation from benzene-pet ether mixture melted at 152-55°.

Decarbonylation of the oxidation product (IV). *formation of 1-methoxy carbazole* (V) : The above oxidation product (40 mg) was mixed with Pd/C (20 mg) and heated in a vacuum sealed tube in presence of 1 ml of dry alcohol for 15 min at 270° The reaction product was taken in benzene-pet ether mixture and allowed to crystallize when 1-methoxy carbazole, m.p. 69-70° was obtained and identified by thin layer chromatography, uv and m.m.p. with an authentic 1-methoxy carbazole.

Na-borohydride reduction of mukolidine : Sodium borohydride (25 mg) was added in cold to a solution

of mukolidine (150 mg) in dry methanol (8 ml). The solution was kept at room temperature for 2 hr On working up the reaction mixture, and crystallisation from benzene-chloroform mixture, homogeneous crystals, m.p. 115-20° were obtained. Identification of this reduction product with natural mukoline was established by comparison of m m p , uv and ir.

Preparation of cyclohexane-1,2-dione-1'-(4-methyl) phenyl hydrazone (**VIII**) : To a solution of 2-formyl cyclohexanone (3.2 g), sodium acetate (5 g) in water was added and the mixture stirred. A diazotised solution of *p*-toludine (3.0 g) at 0-5° was added to it gradually during 40 min. The precipitate (VIII) was filtered, washed and dried. It was crystallised from benzene-petrol mixture, m.p. 205°. [Found : C, 71.90 ; H, 7.21 ; N. 12.30. $C_{13}H_{16}N_2O$ requires C, 72. 22 ; H, 7 40 ; N, 12.49%].

Preparation of 6-methyl-1-oxo-tetrahydro carbazole (**IX**) : The above hydrazone (1.4 g) was added to boiling glacial acetic acid (13 ml). Conc. HCl (3.1ml) was added to it through reflux condenser and the whole mixture was boiled for 3-4 min. The reaction product was poured into ice and stirred. The white crystals of the oxo-compound (IX) appeared which were filtered, washed and dried. It was recrystallized from benzene, m.p. 190°. [Found : C, 64.82 ; H, 6.51 ; N, 7.01. $C_{13}H_{13}NO$ requires C, 65.0 ; H, 6 53 ; N, 7.03%].

Preparation of 1-hydroxy-6-methyl carbazole (**X**) : The above oxo-compound (75 mg) in dry alcohol (5 ml) was dehydrogenated at 250-70° for 4 hr in a sealed evacuated tube in presence of Pd-C catalyst (10% ; 0.7 mg). The reaction product was then made free from catalyst and solvent and the oily residue taken in ether. The ether solution was extracted with 2% alkali. The alkali portion was taken, acidified and again extracted with ether On removal of ether, the residue was taken in benzene, filtered through silica gel bed for purification. Finally, an oily mass was obtained on evaporation of the solvent.

Preparation of 1-methoxy-6-methyl carbazole (**XI**) : The above hydroxy compound (X) in methanol was treated with an ethereal solution of diazomethane at 0-5° and the whole mixture was kept overnight in a refrigerator. After the removal of diazomethane and the solvent, the residue was taken in benzene and crystallised. The crystals were filtered, washed and dried, m.p. 150°. [Found . C, 79.70 ; H, 63.28 , N, 6.42. $C_{14}H_{13}NO$ requires C, 79.59 . H, 6.20 ; N, 6.63%].

Preparation of mukolidine (**IV**) *by DDQ oxidation of 1-methoxy-6-methyl carbazole* (**XI**) : To a stirring solution of 1-methoxy-6-methyl carbazole (40 mg) in benzene, a solution of DDQ (20 mg) in dry benzene was added through a period of 15 min. The stirring was continued for 1/2 hr. The colour of the solution gradually changed from deep green to deep blue. The reaction product was then washed with 1% NaOH and extracted with ether. The ether solution was washed, dried and evaporated The residue was taken in benzene and subjected to preparative thin layer chromatography in the solvent system C_6H_6-$CHCl_3$ (1 : 1). The spot, identical with natural mukolidine, was scraped out from the plate, taken in alcohol, warmed and filtered The filtrate on evaporation gave a solid which on crystallization from benzene furnished homogeneous crystals, m.p 152-55°, identical with mukolidine in all respects (uv, ir, m.p., m.m.p., R_f).

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Synthesis of Pyrano/Pyrido Benzothiophene Derivatives. Part—I

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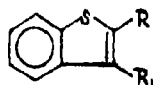
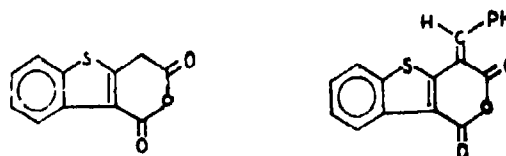
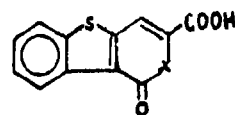
A synthesis of 3-methoxycarbonylbenzo[b]thiophene-2-acetate and 2-formyl-3-methoxycarbonylbenzo[b]thiophene is reported These key compounds have been converted into condensed heterocycles by standard methods.

THE impetus of the work reported herein arose from our success in the synthesis of 1H-pyrano-[3,4-b]benzofuran-1-one derivatives and their 2-aza analogues[1]. Parallel exploratory studies were instituted with benzo[b]thiophene, a description of which forms the subject matter of the present paper.

Benzo[b]thiophene-2,3-dicarboxylic acid (I) which was prepared by a modified method of the earlier published method[2] was esterified with methanolic sulphuric acid to the dimethyl ester, which on controlled hydrolysis afforded the half-ester (II). Alternatively, the half-ester was obtained in good yield by the methanolysis of the anhydride[2] of I. The pmr spectrum of II showed resonances at τ 1.5-2.9 for 4 aromatic protons, and singlets at τ 5 85 (3H, COOCH_3) and τ 3.1 (1H, COOH, exchangable with D_2O). Confirmation of the structure is based on the identification of its decarboxylation product (III) which, on hydrolysis, afforded the known acid[3] (IV). On homologation, the half-ester (II) afforded the di-ester (V) which showed absorptions at 1710 and 1740 cm^{-1}. The related acid (VI) (νCO 1695, 1715 cm^{-1}) was obtained on alkaline hydrolysis. This di-acid, on treatment with acetyl chloride gave the anhydride (IX) which showed carbonyl absorptions at 1745 and 1780 cm^{-1} (the ir data are similar to those observed in homophthalic anhydride).

(I) R = R$_1$ = COOH
(II) R = COOH, R$_1$ = COOMe
(III) R = H, R$_1$ = COOMe
(IV) R = H, R$_1$ = COOH
(V) R = CH_2COOMe, R$_1$ = COOMe
(VI) R = CH_2COOH, R$_1$ = COOH
(VII) R = CH_2OH, R$_1$ = COOMe
(VIII) R = CHO, R$_1$ = COOMe

The di-ester (V) on Stobbe condensation[4] with benzaldehyde gave the related half-ester which, without isolation, was hydrolysed to give α-benzylidene-3-carboxybenzo [b] thiophene-2-acetic acid. This readily furnished the anhydride (X) (νCO 1725, 1759 cm^{-1}) on treatment with acetic anhydride. The ester (V) on condensation with ethyl oxalate[5] followed by the cyclisation of the resulting keto-ester and preferential decarboxylation gave the pyrano carboxylic acid (XI) (νCO 1700, 1730 cm^{-1}). On account of paucity of material (XI) its conversion into XII by ammonia was not possible.

The nitrogen analogue (XII) however was secured from the half-ester (II). The related acid chloride was reduced by $NaBH_4$ in dioxane to the alcohol[6] (VII, ν_{max} 1710, 3420 cm^{-1} ; yield, 67%). Experiments on the oxidation of the alcohol with activated manganese dioxide[7,8] or chromic acid/pyridine[9] led to the formation of I. Dehydrogenation of the alcohol however proceeded smoothly with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[10] when the aldehyde (VIII) was secured in good yield. The aldehydic ester on treatment with hippuric acid, sodium acetate and acetic anhydride gave the related azlactone which on subsequent hydrolysis[11] with alkali gave the pyrido carboxylic acid (XII, νCO 1660, 1700 cm^{-1}).

(IX) (X)

(XI) x = O
(XII) x = NH

Experimental

All m.p s are uncorrected. The infrared spectra were measured as KBr disc and obtained with a Perkin Elmer spectrophotometer, Model 237. The pmr spectrum was recorded in a Varian A-60 apparatus with TMS as internal standard.

Methyl benzo[b]thiophene-2,3-dicarboxylate : A solution of chloroacetic acid (2.84 g) was carefully neutralised with sodium carbonate solution (4 *N*) and added to a solution of benzo[b]thiophene-2,3-dione (4.53 g) in sodium carbonate solution (34 ml ; 2 *N*) at 60-70° and the temperature maintained with stirring for 3 hr. On acidification, benzo[b]thiophene-2,3-

dicarboxylic acid (4.1 g), m.p. 250° separated. This was esterified with methanol (50 ml) containing sulphuric acid (2 ml) for 24 hr. The dimethyl ester crystallised from methanol in stout prisms, m.p. 91° (lit.[a], m.p. 91°).

2-Methoxycarbonylbenzo[b]thiophene-2-carboxylic acid : The foregoing ester (0.5 g) was refluxed with methanolic potash (1.2 ml; 10%) for 25 min. Methanol was removed under reduced pressure and the residue dissolved in water. Any unchanged ester was removed with ether. On acidification and cooling, the half-ester separated as a cream coloured solid. This was collected, dried and crystallised from benzene and obtained as pale yellow needles (0.3 g), m.p. 163°. (Found: C, 55.8; H, 3.4. $C_{11}H_8O_4S$ requires C, 55.9; H, 3.4%).

Alternative method : Benzo[b]thiophene-2,3-dicarboxylic anhydride (m.p. 171°; νCO 1780, 1825 cm^{-1}) (1.0 g) was refluxed with dry methanol (5 ml) for 3.5 hr. The solvent was removed under reduced pressure. The residue taken up in ether and extracted with saturated $NaHCO_3$ solution. This on acidification furnished the half-ester, m.p. 163°, in quantitative yield.

Benzo[b]thiophene-3-carboxylic acid : The foregoing half-ester (0.35 g) was intimately mixed with copper bronze (0.1 g) and the mixture distilled on a metal bath. Methyl benzo[b]thiophene-3-carboxylate (0.28 g) distilled at 165-66°/17 mm. This was hydrolysed without purification by boiling under reflux with sodium hydroxide solution (0.6 ml; 10%) for 1.5 hr. On acidification, the acid was obtained as a colourless solid in quantitative yield, m.p. 175-76° (lit.[a], m.p. 174-75°). (Found: C, 60.4; H, 3.4 $C_9H_6O_2S$ requires C, 60.7; H, 3.4%).

Methyl 3-methoxycarbonylbenzo [b] thiophene-3-acetate : The half-ester (1.4 g) in dry benzene (6 ml) was refluxed with thionyl chloride (2 ml) for 3 hr. Benzene and excess of thionyl chloride were removed under reduced pressure and the resulting crystalline acid chloride (m.p. 61°) in dry ether was added to cooled ethereal diazomethane (from nitrosomethyl urea 6 g) and left overnight in a refrigerator. Removal of the solvent yielded the diazoketone as an oil which was taken up in dry methanol (30 ml) and heated on the water bath with a slurry of silver oxide (0.20 g) in methanol (20 ml) which was added from time to time until the evolution of nitrogen subsided (20 hr). The mixture was clarified by charcoal, filtered and solvent removed. The residue on distillation furnished a pale yellow oil (0.7 g) at 122-28°/0.3 mm which solidified. The ester crystallised from methanol in pale cream needles, m.p. 83°. (Found: C, 58.9; H, 4.5. $C_{13}H_{12}O_4S$ requires C, 59.1; H, 4.6%).

3-Carboxybenzo[b]thiophene-2-acetic acid : The foregoing ester (0.25 g) was hydrolysed by boiling with NaOH solution (1 ml; 10%) for 2 hr. On acidification the related dicarboxylic acid was obtained which crystallised from alcohol in colourless needles, m.p. 235° (evolution of gas). (Found: C, 55.8; H, 3.4. $C_{11}H_8O_4S$ requires C, 55.9; H, 3.4%).

Anhydride. Pyrano(4,3-b)benzothiophene-1,3-(1H,3H,4H)-dione : This was obtained by heating the dicarboxylic acid (0.1 g) with acetyl chloride (2 ml) for 4 hr. This crystallised from dry benzene in cream coloured needles, m.p. 204-5°. (Found: C, 60.5; H, 2.7. $C_{11}H_6O_3S$ requires C, 60.6; H, 2.8%).

α-Benzylidene-3-carboxybenzo[b]thiophene-2-acetic acid : A mixture of freshly distilled benzaldehyde (0.22 g) and methyl 3-methoxycarbonylbenzo[b]thiophene-2-acetate (0.53 g) was added to alcoholic sodium methoxide (sodium 0.05 g, methanol 4 ml) and refluxed for 6 hr. The residual mass after the removal of solvent was dissolved in water, extracted with ether to remove unchanged ester and then boiled with the addition of aqueous sodium hydroxide (3 ml, 10%) for 2 hr, cooled, and acidified. The sticky mass solidified on trituration with benzene. The compound (0.54 g) crystallised from alcohol in yellowish needles, m.p. 208° (evolution of gas). (Found. C, 66.5, H, 3.7. $C_{18}H_{12}O_4S$ requires C, 66.7, H, 3.7%).

The anhydride was obtained by heating the dicarboxylic acid (0.1 g) with acetic anhydride (2 ml) for 10 min. This crystallised from benzene in deep yellow needles (0.06 g), m.p. 195°. (Found: C, 70.4; H, 3.2 $C_{18}H_{10}O_3S$ requires C, 70.6; H, 3.3%).

Condensation with ethyl oxalate : A mixture of ethyl oxalate (0.17 g) and methyl 3-methoxycarbonylbenzo[b]thiophene-3-acetate (0.27 g) was added to alcohol free sodium ethoxide (from sodium, 0.03 g) in dry benzene when the colour turned brown. The mixture was left overnight in the refrigerator and next day, dilute sodium hydroxide solution (1 ml; 1 *N*) followed by ether was added to it. The alkaline solution was separated, acidified and extracted with ether. On removal of the solvent the glyoxalyl derivative separated as an oil which was dissolved in acetic acid (0.5 ml) and treated with concentrated hydrochloric acid (0.25 ml), warmed on the water bath for 30 min and cooled. After removal of volatile matter under reduced pressure, the brownish oily residue (0.15 g) was refluxed with a mixture of acetic acid (1.5 ml) and conc. hydrochloric acid (0.8 ml) for 3 hr. A brown solid separated on cooling which was crystallised to give pyrano(4,3-b)-benzothiophene-1-oxo-3(1H)-carboxylic acid which separated from alcohol in pale brown needles (0.1 g), m.p. 272°. (Found: C, 58.3; H, 2.3. $C_{12}H_6O_4S$ requires C, 58.6, H, 2.5%).

Methyl 2-Hydroxymethylbenzo [b] thiophene-3-carboxylate : A solution of the half-ester (1.2 g) in dry benzene (5 ml) was refluxed with thionyl chloride (2 ml) for 3 hr. On removal of solvent, the resulting acid chloride was taken up in dry dioxane (0.8 ml) and added in instalments to a suspended mass of sodium borohydride (0.29 g) in dioxane (5 ml) with efficient stirring and left overnight with continuous stirring. Next day, the mixture was heated on a water bath for 8 hr, cooled and the complex decomposed carefully with iced dilute hydrochloric acid. The resulting oil was taken up with ether, washed with $NaHCO_3$ solution and dried.

On removal of the solvent, the alcohol solidified. This crystallised from alcohol in colourless wooly needles (0.8 g), m.p. 193°. (Found : C, 59.5 ; H, 4.4. $C_{11}H_{10}O_3S$ requires C, 59.5 ; H, 4.5%).

Methyl 3-formylbenzo[b]thiophene-3-carboxylate : The foregoing alcohol (0.66 g) in dry benzene (10 ml) was refluxed with DDQ (0 68 g) for 30 min and filtered hot On removal of the solvent the aldehydic ester was obtained as a darkish oil. The 2,4-DNP crystallised from acetic acid as orange needles, m p. 254-55° (decomp). (Found N, 13.9. $C_{17}H_{12}O_6N_4S$ requires N, 14 0%)

Azlactone : The foregoing aldehyde (0.45 g) was mixed with hippuric acid (0.5 g), fused sodium acetate (0.2 g) and acetic anhydride (1.2 ml). The mixture was heated on the water bath for 3 hr, cooled and filtered. The residue thus obtained was washed with alcohol affording the azlactone crystallising from acetic acid in silky yellow needles (0.35 g), m.p 228° (Found: C, 66.0 ; H, 3.6 ; N, 3.8. $C_{20}H_{13}O_4NS$ requires C, 66.1 . H, 3 6 ; N, 3.9%).

Pyrido (4,3-b)benzothiophene-1-oxo-3(1H, 2H)-carboxylic acid : The foregoing oxazolone (0.25 g) was heated with potassium hydroxide solution (4 ml ; 10%) for 2 hr. The clear yellow solution was cooled and acidified. The cream coloured solid which separated was washed with hot water and dried (0.16 g). The compound crystallised from acetic acid in creamy needles, m.p. 354° (decomp) (Found : C, 58.5 ; H, 2.7 ; N, 5.7. $C_{12}H_7O_3NS$ requires C, 58.8 ; H, 2.9 ; N, 5.7%).

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Some Aspects of the Chemistry of Fluorinated 1,3-Diketones*

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Some aspects of the chemistry of fluorinated 1,3-diketones have been discussed viz., their interdisciplinary nature, analytical applications, enolic content, metal 1,3-diketonates and their quasi-aromatic character, use as laser chelates, nmr shift reagents and synthetic applications for formation of bioactive heterocycles

THE chemistry of fluorinated 1,3-diketones and related compounds has received considerable attention in recent years in view of their interdisciplinary significance and diverse uses. 1,3-Diketones (or β-diketones) are carbonyl compounds in which the two carbonyl groups are separated by a methylene or a substituted methylene group. The introduction of perfluoro groups in such systems imparts interesting and novel properties to these compounds. Some of these are indispensable reagents in analytical chemistry and the most recent uses are in analysing lunar samples[1], cobalt in vitamin B_{12}[2] and detection of other trace elements in blood, serum and other essential biological materials[3]. The fluorinated 1,3-diketones possess excellent complex forming properties and thenoyltrifluoroacetone (TTA), furoyltrifluoroacetone (FTA), thiothenoyltrifluoroacetone (STTA) and heptafluorobutanoylpivalyl methane[4] (FOD) are some of the well known agents.

Synthetic routes for fluorinated 1,3-diketones are similar to those for non-fluorinated diketones with certain exceptions. One review[5] has recently appeared on fluoro 1,3-diketones and lists the important methods. We have synthesised a number of new polyfluorinated 1,3-diketones using Claisen condensation[6-7]. This involves a base prompted condensation of a fluorinated ester with a ketone containing at least one alpha hydrogen Sodium amide and sodium hydride have been employed as condensing agents with benzene or diethyl ether as solvent. Keto-enol tautomerism is a general characteristic of these diketones. The tautomerism of 1,3-diketones has been studied in detail by deuterium exchange reaction, Raman effect, polarographic oxidation-reduction and by spectral studies, viz., ir, uv and pmr.

The effects of fluorine substitution on enolization have been studied by Park *et al*[8]. Unlike the non-fluorinated 1,3-diketones (e.g. acetylacetone), hydrogen bonding is possible in both *syn* as well as in *anti* forms in fluorinated 1,3-diketones (e.g. trifluoroacetylacetone) (Fig. 1). This explains the very high enolic content of fluorinated 1,3-diketones. In fact, ir spectra of such ketones donot show characteristic >C=O absorption band (1725-1708 cm^{-1}). Further, intramolecular as well as intermolecular

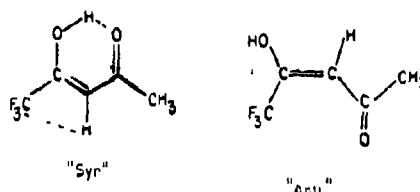



Fig 1 Hydrogen bonding in fluorinated 1,3-diketones

hydrogen bonding are observed in the regions 2700 2500 and 3000-2900 cm^{-1}, respectively. In nmr spectra, the presence of =CH– resonance signal in the region δ 6.2-6 1 ppm and enolic proton resonance signal in the region δ13-26 ppm provide substantial support for the enolization of such compounds. The role of various substituents on the degree of enolization has been studied by us[6]. The enolic content of our fluorinated β-diketones vary considerably in the range 54.73-100%. On substitution of highly electronegative groups, such as CF_3 or C_2F_5, the enol content increases as the chelate is stabilized by O–H . O and O–H ..F intramolecular bonds. Substitution of phenyl groups at 1 or 3 or both positions, in place of CH_3 group, also increases the enol percentage. It is ascribed to the stabilization of the enol tautomer due to the phenyl ring being coplanar with the enol ring and thus enabling electrons to be supplied to the enol chelate ring through resonance.

Metal 1,3-diketonates :

The chemistry of the fluorinated metal 1,3-diketonates has aroused much recent interest in laser devices[9], as nmr shift reagents[10] and in analytical chemistry[11]. Under appropriate conditions, the enolic proton of a 1,3-diketone can be replaced by different metals or their salts, forming a metal derivative which is a characteristic of 1,3-diketones (Fig. 2). Several reviews have appeared on metal 1,3-diketonate complexes and only two on fluorinated 1,3-diketonates.

*Dedicated to Prof. Arun K. Dey on the occasion of his 60th birth day.

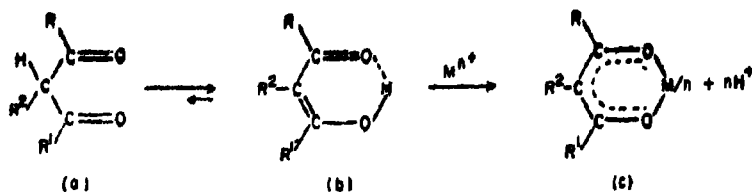
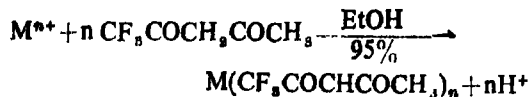



Fig. 2. Tautomers of 1,3-diketone : (a) and (b) ; metal 1,3-diketonate : (c).

The addition of a concentrated metal salt solution to an aqueous methanolic or aqueous ethanolic solution of fluorinated 1,3-diketones results in precipitation of metal chelates.

$$M^{n+} + n\, CF_3COCH_2COCH_3 \xrightarrow[95\%]{EtOH} M(CF_3COCHCOCH_3)_n + nH^+$$

The metal salts usually used are acetate, nitrate, oxalate, oxychloride and chloride. The other well-known methods for preparing such compounds have been reviewed by us[15]. Some of the metal-diketonates studied by us are those derived from Cu^{2+}, Cr^{3+}, Eu^{3+}, Sm^{3+}, Tb^{3+} and Gd^{3+}.

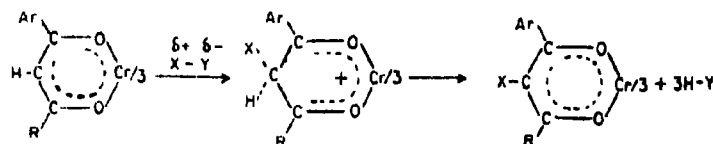
Quasi-aromatic character :

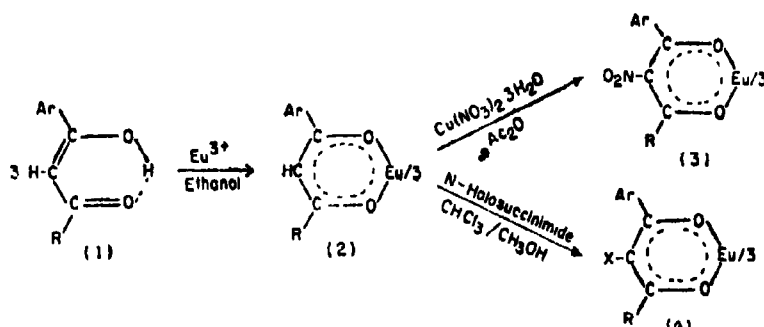
According to Collman *et al*[16] and other workers[17], each chelate ring in metal 1,3-diketonates has a cyclic π-orbital, formed by the overlapping of vacant d-orbital of the central metal atom of the 1,3-diketonate. These systems have been found to undergo typical electrophilic substitution reactions of the hydrogen atom linked to sp^2 hybridized carbon atom and the metal 1,3-diketonates have been termed as quasi-aromatic.

The presence of a perfluoroalkyl group, with its accompanying inductive effect, makes electrophilic substitution slower and requires forcing conditions. We have been able to accomplish this in case of fluorinated 1,3-diketonato chromium derivatives synthesised by us and chloro-, bromo- and nitro-substituents have been introduced at the central carbon atom of the chelate ring under carefully controlled conditions[18] (Scheme 1)

The quasi-aromaticity of transition metal 1,3-diketonates is well established by now but the quasi-aromatic nature of lanthanide 1,3-diketonate was not investigated. We have, therefore, investigated this problem[19-21] and have reported that like the transition metal 1,3-diketonates, the lanthanide 1,3-diketonato system also behaves like a sensitive heterocycle possessing some aromatic character (Scheme 2).

On the basis of results obtained, it can be stated that the degree of delocalisation of π-electrons in lanthanide 1,3-diketonates is more pronounced than in the transition metal system leading to enhanced quasi-aromaticity.

The methine proton at the central carbon atom of the chelate ring has been subjected to nitration, chlorination and bromination. Substitution in the phenyl ring is unlikely because of ring deactivation from electron release resonance effects. The disappearance of the C-H in-plane bending vibration band from the region 1225-1180 cm^{-1} in the ir spectra and the disappearance of the methine resonance signal from the region δ 6.2 ppm in the pmr spectra provide strong evidence for electrophilic substitution at the central carbon atom.

Ar = 4-FC_6H_4 or a derivative, X = Cl, Br, or NO_2, R = Me, Et, Pr^n, CF_3 or Ph.

Scheme 1

Ar = Fluoroaryl group ; R = CH_3, C_2H_5, CF_3, C_2F_5 or nC_3F_7 ; X = Cl, Br.

Scheme 2

Laser chelates :

Since Urbain's work[22] on the rare earth 1,3-diketonates, the chemistry of such compounds has assumed considerable importance because of their practical use as potential laser materials. The first laser action from europium benzoylacetonate at 6130 Å was reported by Lempicki and Samelson[23] and Schimitschek[24]. Bhaumik *et al*[25] have shown that laser activity is possible only with tetrakis chelates of rare earth and not with *tris* chelates. One of the more successful ligands, so far investigated is benzoyltrifluoroacetone. Its tetrakis derivative, $Eu(BTFA)_4Q$, where Q is a cation (Fig. 3), has been shown to lase in acetonitrile solution from 77K to an unusually high temperature (i.e room temperature). We have studied[26,27] new tetrakis rare earth chelate salts of the type piperidinium$^+$ $[(ArCOCHCOR)_4M]^-$ (where Ar= fluorophenyl or substituted fluorophenyl, R= alkyl, aryl or perfluoromethyl and M=La^{3+}, Pr^{3+}, Nd^{3+} and Eu^{3+}). Some of these complexes have been examined for their fluorescence in the solid state at 77K. The $^5D_0 \rightarrow {}^7F_2$ (at 6173 Å) is by far the most intense transition in case of europium chelates accounting for approximately 95% of the total emission in all europium chelates. It may be noted that this is the first case of piperidinium tetrakis-europium-1,3-diketonates in which the $^5D_2$ level has been observed to fluoresce.

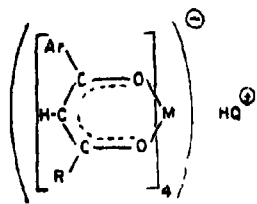



Fig. 3. Ar = Fluoroaryl group ;
R = Alkyl, aryl or perfluoroalkyl group.
M = Eu^{3+}, Sm^{3+}, Tb^{3+}, Gd^{3+}, La^{3+}, Pr^{3+} or Nd^{3+}
Q = Piperidine.

The terbium complex showed fluorescence at 5800 Å (overlapped with the transition of Eu^{3+}) and 5440 Å, involving $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_5$ transitions, respectively. In the samarium complex, fluorescence was observed at 5640 Å due to $^4F_{3/2} \rightarrow {}^6H_{7/2}$ and at 5980 Å due to $^4G_{5/2} \rightarrow {}^6H_{9/2}$. The line emission in the samarium chelate is very faint but distinct from europium line emission. The uv absorption spectra[27] reveal two maxima. The first maximum is in the region of 3250-3570 Å and is a bathochromic shift of the 1,3-diketone anion absorption due to coordinated chelate ion formation. This clearly indicates that all four 1,3-diketone molecules are used in chelate formation with the metal ion. The second maximum in the region of 2440-2600 Å may be due to free 1,3-diketone anion whose formation in solution is ascribed to ionisation of the original tetrakis chelates as follows :

$$(L)_4\,MHP \rightleftharpoons L_3M + L^-HP^+_3$$

where L=ligand, M=rare earth metal, HP^+= piperidinium ion.

NMR shift reagents :

In 1969, Hinckley[10] discovered that the addition of *bis* pyridine adduct of *tris* dipivalomethanato europium, $Eu(dpm)_3.2Py$ to a carbon tetrachloride solution of cholesterol caused important selective downfield shifts in nmr spectrum of steroid and for obvious reasons, the europium complex was named as "shift reagent". The discovery at once suggested that it could lead to simplification of spectra by removal of signal coincidence and also characterization of nucleus in terms of its geometrical relationship with respect to one or more distant functional groups.

The paramagnetic *tris*-lanthanide(III) chelates of H(fod) $Ln(fod)_3$ have been increasingly used as nmr shift reagents since the first report. The chemical property which permits this application is the Lewis acidity possessed by the chelates as a consequence of their coordinative unsaturation. The neutral *tris*-chelates dissolve in organic solvents and form labile adducts with a large variety of nucleophilic substrates. Lewis acidity of these chelates also causes two side interactions which may interfere with their usage as nmr shift reagents.

Eu(III) chelates of fluorinated 1,3-diketones e.g., H(fod) and H(tfacam) undergo[28] much stronger interactions with nucleophiles (ethers, ketones, alcohols, esters and olefins) than similar non-fluorinated Eu(III) chelates. This is most probably due to the increased acidity of the fluorinated chelates due to a decrease in the basicity of the fluorinated 1,3-diketones, and to increased solubility. $Eu(fod)_3$ is probably the best overall shift reagent for spectral clarification presently available.

Very recently (1974), a novel and efficient nmr shift reagent, tetrakis(1,1,1-trifluoro-4-phenylbutane-2,4-dionato) uranium, $U(btfa)_4$, has been prepared[29]. It is capable of forming adducts with Lewis bases (e g Py and *n*-BuOH) and inducing proton shifts of a magnitude similar to those obtained with $Eu(dpm)_3$.

We have also recently synthesised some new polyfluorinated lanthanide 1,3-diketonates[30] and have studied their ability to produce shifts[31] in *n*-hexanol, *n*-heptanol, *n*-dodecanol, *p*-fluoroaniline and *m*-trifluoromethyl aniline. The following compounds have been examined :

1. [4,4,5,5,5-Pentafluoro-1-(fluorophenyl) 1,3-pentanedionato]holmium(III).
2. [4,4,5,5,6,6,6-Heptafluoro-1-(4′-fluorophenyl) 1,3-hexanedionato]europium(III).
3. [4,4,5,5,6,6,6-Heptafluoro-1-(4′-fluorophenyl) 1,3-hexanedionato]praseodymium(III).
4. [4,4,5,5,5-pentafluoro-1-(4′-fluorophenyl) 1,3-pentanedionato]praseodymium(III).

It was observed that europium and praseodymium 1,3-diketonates act as the best shift reagents for downfield and upfield shifts, respectively as they donot produce line broadening. Holmium 1,3-diketonates produce maximum shifts with certain nucleophiles but they are not used as shift reagents due to line broadening.

As reaction intermediates for synthesis of bioactive heterocycles :

Apart from the various analytical applications of the 1,3-diketones listed above, we have recently employed these compounds for synthesis of different types of bioactive heterocycles containing fluorinated groups. These heterocycles include pyrazoles, isoxazoles, pyrazolo[1, 5-a]pyrimidines, 1, 2, 4-triazolo[4, 3-b]pyridazines, 1H-pyrazolo[3, 4-b]-pyridines, 1,4-diazepines, 1,5-benzodiazepines, pyrazolo, [5,1-c][1, 2, 4] triazines etc. Some of these compounds have shown promising CNS depressant, antiobesity and anticholinergic activities[31].

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Restricted Rotation. Part—IV : Determination of Barrier to Rotation Around Some Crowded C-C and C-N Bonds by Dynamic Nuclear Magnetic Resonance

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Temperature dependence of the nmr spectra of a few typical methyl 2-aryl-6-oxocyclohex-1-enyl-acetates (I)-(VII) has been reinvestigated. The free energy, enthalpy and entropy of activation for the restricted rotation about the arylcyclohexenone bond have been determined by line shape analysis of the spectra of the side chain methylene protons using approximate equations. The free energy of activation for conformational inversion of the molecule (VII) is now found to be appreciably higher than that reported earlier although the result is still to be rationalised. The barrier energy around C-N bond in two 1-aryl-1,4 dihydro-4,4,6-trimethyl-2-thiopyrimidones (XIII) and (XV) has also been measured by dynamic nmr taking advantage of chemical nonequivalence of the geminal methyl groups and is found to be quite high (*ca* 98 kJ mol^{-1}).

SINCE its discovery, the high resolution nmr spectroscopy has become one of the most valuable tools of the chemists, biochemists and physicists for the determination of structures of molecules. In addition to the static aspects of the molecules (e. g., chemical shifts, coupling constants), nmr is capable of giving valuable information on many time-dependent phenomena which include a large number of exchange reactions characterised by certain rate constants[1]. Rotation about a single bond may be visualised as an intramolecular stereodynamic process in which the rate constant depends on the barrier energy. Previously, molecules like biphenyls with restricted rotation around the pivotal bond had to be resolved into enantiomers in order to study the barrier energy and polarimetry was the sole method of investigation. Nowadays, it is possible to study the hindered rotation by means of dynamic nmr when the energy barrier is just on the border line (75-96 kJ mol^{-1}), where compounds become too unstable to be isolated chemically, down to a barrier of 21-25 kJ mol^{-1} below which another powerful tool, namely, microwave spectroscopy can be applied. Moreover, unlike polarimetry, it is not necessary that the two conformers should be enantiomeric and possess a chiral centre or axis. In principle[2], if a molecule by reason of restricted rotation happens to lack certain symmetry properties so that two conveniently placed groups (generally H or Me) become diastereotopic, the technique of dynamic nmr may be used to determine activation energies of the rotational process. A large number of biphenyl derivatives and their analogues have been studied using this method by various groups of workers[3]. In our laboratory, a dozen of 3-arylcyclohexenones of the type (I) have been synthesised and the free energies of activation of restricted rotation about the arylcyclohexenone bond determined[4-6] from the coalescence temperature of the AB-quartet of the diastereotopic protons in the acetate side chain. In the absence of full line shape analysis[1], the measurements were, however, confined to the calculation of free energies of activation ($\Delta G^{\neq}$) for conformational inversion at the coalescence temperature (T_c). The significance of the values was limited by the fact that their temperature dependence was not known. In the present communication, a few typical molecules (I)-(VII) have been re-examined by line shape analysis using approximate equations, the enthalpy and entropy of activation have been calculated and compared, and the temperature dependence of free energies of activation has been studied. The compound (VII) which behaved atypically[5] has been synthesised eliminating any controversy over its structure. In addition, the barrier to rotation about C-N bond in some 1-aryl-1,4-dihydro-4,4,6-trimethyl-2-thiopyrimidones[7] has been determined by dynamic nmr.

Experimental

^{1}H NMR spectra at different temperatures were taken on a Varian EM390 90 MHz machine. Temperature control was provided by a Varian variable temperature controller with an accuracy of ±2°. Temperatures above 50° were calibrated using the shift difference of an ethylene glycol sample. Chemical shifts are reported in ppm relative to TMS as internal standard. IR spectra were taken in $CHCl_3$ solution on Perkin-Elmer 237B spectrometer. Petroleum refers to a fraction, b.p. 40-60°. Organic solutions were dried over anhydrous Na_2SO_4. All

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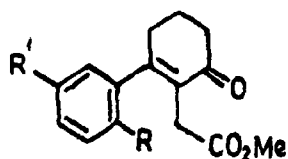
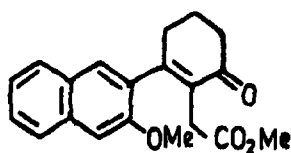

I : R = OMe, R' = H

II : R = Me, R' = H

III : R = R' = Me

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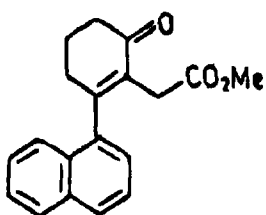
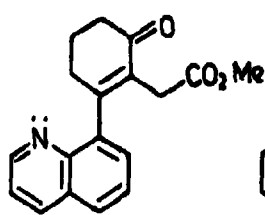
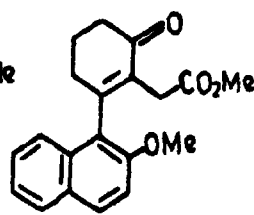
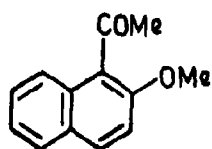
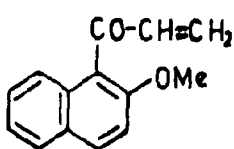
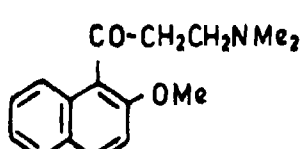
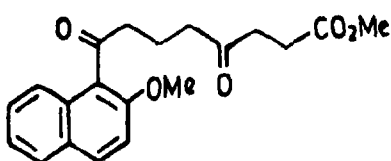
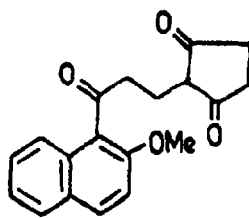
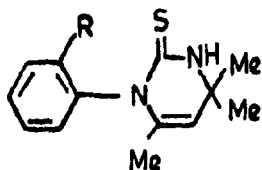

V VI VII

VIII IX X

XI XII

XIII : R = OMe

XIV : R = Me

XV : R = NO_2

the melting points are corrected. TLC was done on silica-gel plates using ethyl acetate and petroleum as eluents.

Methyl 2-aryl-6-oxocyclohex-1-enylacetates (I)-(VI) were prepared by method described earlier[4,5]. The synthesis of compound (VII) has been carried out with some modification as described below and the intermediates are carefully checked by tlc, glc and ^{1}H nmr for their purity.

1-Acetyl-2-methoxynaphthalene (VIII) : 1-Acetyl-2-methoxynaphthalene was prepared according to the previous method[4] and was rigorously purified by

column chromatography (silica gel). It crystallised from petroleum in colourless plates, m.p. 58°; ^1H nmr spectrum ($CDCl_3$): δ 8.00-7.80 (3H, m, 3×ArH), 7.60-7.20 (3H, m, 3×ArH), 3.95 (3H, s, OCH_3) and 2.63 (3H, s, $COCH_3$); ν_{max} : 1695 and 1600 cm^{-1}. The ^1H nmr spectrum ($CDCl_3$) of 1-acetyl-2-naphthol[8] is as follows: δ 13.55 (1H, s, exchangeable with D_2O, -OH), 8.17 (1H, d, J=8 Hz, 8-H), 8.07-7.30 (4H, m, 4×ArH), 7.20 (1H, d, J=8 Hz, 3-H) and 2.87 (3H, s, $COCH_3$); ν_{max} : 1630 and 1580 cm^{-1}. Each of these compounds gave a single spot and a single peak in tlc and glc (FAAP 15% column), respectively.

Attempted preparation of 2-methoxy-1-naphthyl vinyl ketone (**IX**) *with trifluoroacetic acid N-methylaniline salt* (*TAMA*): Recently, a new procedure has been developed[9] to synthesise α-methylene ketones using 'TAMA' and trioxymethylene Accordingly, a mixture of 'TAMA' (2.25 g), 1-acetyl-2-methoxynaphthalene (2.00 g) and trioxymethylene (1.08 g) in dry freshly distilled dioxane (12 ml) was refluxed under N_2 for 2 hr followed by heating with fresh amount of trioxymethylene (0.51 g), 'TAMA' (1.2 g) and dioxane (6 ml) for 2 hr more. The ketone (**VIII**) was, however, recovered completely unchanged. Apparently, the method does not work with sterically hindered ketones[9].

Methyl 7-(2-methoxy-1-naphthoyl)-4-oxoheptanoate (**XI**) : This compound was prepared by condensing the Mannich base of 1-acetyl-2-methoxynaphthalene methiodide with ethyl β-oxo-adipate[10] as described in a previous paper[4]. 2-Methoxy-1-naphthyl β-NN-dimethylaminoethyl ketone (X), prepared in the usual way had the ^1H nmr spectrum ($CDCl_3$): δ 8.05-7.70 (3H, m, 3×ArH), 7.60-7 20 (3H, m, 3×ArH), 3.97 (3H, s, OCH_3), 3 13 (2H, m, $COCH_2$), 2.83 (2H, m, CH_2NMe_2) and 2.27 (6H, s, NMe_2); ν_{max} : 1695 and 1610 cm^{-1}. The dioxo-ester (**XI**) showed ^1H nmr ($CDCl_3$) : δ 8.00-7.55 (3H, m, 3×ArH), 7.50-7.20 (3H, m, 3×ArH), 3.92 (3H, s, OCH_3), 3.63 (3H, s, CO_2CH_3), 2 92 (2H, *t*, J=7 Hz, 3-CH_2), 2.60 (6H, m, 3×CH_2CO) and 2.06 (2H, m, 6-H_2); ν_{max} : 1735 (CO_2Me), 1719 (satd. C=O), 1695 (ArCO) and 1610 cm^{-1} (aromatic). The dioxo-ester (**XI**) was a viscous gum, b.p. 220-225°/0.1 mm. Found : C, 70.3 : H, 6.6. $C_{20}H_{22}O_5$ requires C, 70.2 ; H, 6 4%.

Methyl 2-(2-methoxy-1-naphthyl)-6-oxocyclohex-1-enylacetate (**VII**) : The above dioxo-ester (1.4 g ; 4.1 mmol) was added to a solution of dry potassium *t*-amylate, prepared from potassium (0.16 g ; 4.1 mmol), in benzene (30 ml) The solution was refluxed on a water-bath for 5 hr under N_2. Some salt precipitated out. The cooled mixture was decomposed with dilute acid and the organic matter was extracted with ether. The ethereal layer was washed repeatedly with aqueous $NaHCO_3$ solution when 2-(2-methoxy-1-naphthyl)-6-oxocyclohex-1-enylacetic acid (hydrolysed from the cyclised ester by the liberated water during aldol condensation) came up completely into the alkaline layer. On acidification, a gum (0 85 g) was obtained which was esterified with diazomethane and the ester sublimed at 200°/0 1 mm. The product was mostly methyl 2-(2-methoxy-1-naphthyl)-6-oxocyclohex-1-enylacetate (VII) admixed with a little amount (*ca* 20% as determined from nmr) of the methyl ether of the cyclopenta-1,3-dione derivative (**XII**) formed as a result of internal Claisen condensation. The product was chromatographed over silica-gel when the cyclohexenylacetate (VII) was obtained in crystalline form, m p. 102° (from benzene petroleum). Found . C, 74 4 . H, 6 7. $C_{20}H_{20}O_4$ requires C, 74.1 ; H, 6 2%; ^1H nmr spectrum ($CDCl_3$) : δ 8.00-7 31 (7H, m, ArH), 3.90 (3H, s, OCH_3), 3 42 (3H, s, CO_2CH_3), 3 00 (2H, AB–q, CH_2CO_2-Me), 2.65 (4H, m, 3–H_2+5–H_2) and 2.26 (2H, m, 4–H_2). In $C_6D_5NO_2$, the side chain quartet at δ 3.00 appeared as a singlet but in $CDCl_3$ (up to 60°) and in Cl_2C=CCl_2, the quartet was retained.

The ester formed a red dinitrophenylhydrazone, m.p 216° (reported[5] m p. 216-217°). Found : C, 62.1 ; H, 5.1 ; N, 11·0. $C_{26}H_{24}N_4O_7$ requires C, 61.9 ; H, 4.8 ; N, 11.1% ; ^1H nmr spectrum

TABLE 1—NMR PARAMETERS[a] AND ENERGIES[b] OF ACTIVATION OF ROTATION ABOUT THE ARYL-CYCLOHEXENONE BOND IN COMPOUNDS (I)-(VII)

Compound	Solvent	J_{AB} Hz	$\Delta\nu_{AB}$ Hz	T_c °C	k_c	$\Delta G^{\ddagger}_c$	$\Delta G^{\ddagger c}_c$	$k_{100°}$	$\Delta G_{100°}$	$k_{180°}$	$\Delta G^{\ddagger}_{180°}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$ e.u.
I	$C_6D_5NO_2$	15.00	16.10	45	89.15	66 05	67 80	630	71 90	–	–	50.24	–11
	o-$C_6H_4Cl_2$	24.00	25.88	50	142 60	64 08	–	620	72.00	–	–	46 00	–13
II	$C_6D_5NO_2$	16.50	17.43	145	97 80	87 45	88 41	–	–	700	87.60	95 14	+ 4
III	$C_6D_5NO_2$	16.50	17.43	145	97 80	87.50	88 60	–	–	710	87 66	96 39	+ 5
IV	$C_6D_5NO_2$	17.00	20.98	62	110.40	69.10	69 80	640	71 80	–	–	52.67	–12
V	$C_6D_5NO_2$	16.50	19.45	184	99.70	95.85	95 30	–	–	–	–	–	–
VI	$C_6D_5NO_2$	17.00	40 60	95	129 20	75.49	75.80	380	76 20	–	–	65.25	– 6
VII	Cl_2C=CCl_2	17.00	10.50	80	95.50	73.15	66.00	160	74 17	–	–	53 50	–11

[a]The spectral changes are reversible with temperature [b]Energy is expressed in kJ mol^{-1} ; the maximum errors are estimated for $\Delta G^{\ddagger}$ to be ±1.0 kJ mol^{-1} ; for $\Delta H^{\ddagger}$ to be ±4 kJ mol^{-1}, and for $\Delta S^{\ddagger}$ ± 4 e.u mol^{-1}. [c]Data taken from refs. 5, 6.

($CDCl_3$) : δ 11.2 (1H, s, ArNH), 9.23 (1H, d, J= 3Hz, 3′–ArH), 1.60 (1H, 2×d, J=9 and 3 Hz, 8–ArH), 8.10-7.30 (7H, m, ArH), 3.94 (3H, s, OCH_3), 3.50 (3H, s, CO_2CH_3), 3.17 (2H, AB–q, J=17 Hz, Δν=10 Hz, CH_2CO_2Me), 2.80 (2H, t, J=7 Hz, 5–H_2), 2.60 (2H, t, J=7 Hz, 3–H_2) and 2.24 (2H, m, 4–H_2).

1-Aryl-1,4-dihydro-4,4,6-trimethyl - 2 - thiopyrimidones (XIII)-(XV) : These thiones were prepared by a one step procedure from the corresponding aromatic amines, 4-methylpent-3-en-2-one (mesityl oxide), ammonium thiocyanate, water and hydrochloric acid as reported[11,12]. These compounds have been characterised by us (ir, nmr) elsewhere[7].

Results and Discussion

The nmr spectra of the seven arylcyclohexenones (I)-(VII) showed an AB-quartet (first three lines were clearly discernible in all the spectra) for the diastereotopic methylene protons of the acetate side chain. The J_{AB} and Δν values were calculated from the positions of the first and second, and first and third lines respectively according to standard procedure[5]. At coalescence temperature (T_c), each quartet coalesced to a broad singlet which gradually sharpened with increased temperature. The approximate exchange rate, k_c, and the free energy barrier to configurational inversion, $\Delta G_c^{\ddagger}$, at T_c were calculated by using equations (1) and (2), respectively[10]. At several temperatures above T_c, the line widths of the coalesced singlet at its half height (W/Hz) were measured and the approximate inversion rates were obtained over a range of temperatures by equation (3)[14,15] where W_0 is the half width of the singlet at the highest temperature attainable. When k was plotted against 1/T (T in absolute scale), an approximate linear relationship

$$k_c = \pi[(\Delta\nu^2_{AB} + 6\ J_{AB}^2)\ 2]^{\frac{1}{2}} \quad . \quad (1)$$

$$\Delta G_c^{\ddagger} = 4.57 \times T_c\ (10.32 + \log \frac{T_c}{k_c}) \quad . \quad (2)$$

$$k = \frac{\pi \Delta\nu^2_{AB}}{2(W - W_0)} \quad \ldots \quad (3)$$

$$\Delta H^{+} = E_a - RT \quad \ldots \quad (4)$$

$$\Delta S^{+} = \frac{\Delta H^{+} - \Delta G^{+}}{T} \quad \ldots \quad (5)$$

was observed which permitted the determination of the values of ΔG^{+} at different temperatures with some degree of accuracy. Arrhenius parameter, E_a, was measured from the slope of the straight line when log k was plotted against $\frac{1}{T}$ and from E_a, ΔH^{+} and ΔS^{+} were calculated using equations (4) and (5). The results are summarised in Table 1.

TABLE 2—NMR PARAMETERS[a] AND FREE ENERGIES OF ACTIVATION OF ROTATION ABOUT C-N IN COMPOUNDS (XIII) AND (XV)

Compound	Solvent	Δν Hz	T_c °C	k_c	ΔG_c^{+} kJ mol⁻¹
XIII	$C_6D_5NO_2$	1.5	140	3.33	97 90±0.2
	o-$C_6H_4Cl_2$	2 4	150	5.33	98.73±0.2
XV	$C_6D_5NO_2$	3.0	160	6.67	100.24±0 2

[a]The spectral changes are reversible with temperature

It may, however, be noted that the enthalpy and entropy of activation derived from nmr line shape analysis using approximate equations are subject to large systematic errors[16]. Consequently, the significance of the values of ΔH^{+}, ΔS^{+} and the observed temperature dependence of ΔG^{+} are very much doubtful and no serious conclusion should be drawn therefrom. The following points are observed from the results presented in Table 1 which also contains data of our previous work[5] for comparison.

i) The coalescence temperature, T_c, and free energy of activation, $\Delta G_c^{\ddagger}$, of the 2-methoxy-1-naphthyl derivative (VII) have now considerably increased. The former is found to be 80° instead of 45° and the latter 73.15 instead of 66.00 kJ mol⁻¹, determined in tetrachloroethylene. The AB-quartet remained intact in chloroform solution upto 60° which shows that the previous measurement (done in a foreign laboratory) was wrong. The $\Delta G_c^{\ddagger}$ value (73.15 kJ mol⁻¹) is still very much less than that (95.30 kJ mol⁻¹) for the 1-naphthyl-derivative (V). We reiterate our previous explanation[5] that the ground state energy of the molecule (VII) is appreciably increased by the o-methoxy substituent while that of the transition state may have been reduced by a combined effect of conjugation and out-of-plane bending of the pivotal bond both assisted by methoxyl group[17,18]. It must be understood that unlike the biphenyl derivatives, where both the rings are planar, the cyclohexenone moiety in VII is nonplanar and may have different conformations in the ground and the transition states leading to different steric interactions. The $\Delta G_c^{\ddagger}$ values of the rest of the compounds agreed with those previously reported[5].

ii) Although the measurement of ΔH^{+} and ΔS^{+} values are very much unreliable for reasons stated earlier, there is an unmistakable trend towards high negative entropy of activation (−11 e.u.) and low ΔH^{+} values for compounds (I), (IV) and (VII) which contain an *ortho*-methoxyl group. On the other hand, the three compounds (II), (III) and (V) having no methoxyl substituent show very small (almost negligible) positive entropy of activation and their ΔH^{+} values are comparable with those of ΔG^{+}. It is risky to draw any firm conclusion based on this very uncertain ground; we can only conjecture that the rotation of the methoxyl group *ortho* to the pivotal bond is much more restricted (and therefore more orderly) in the transition state than in the ground

state, which explains this negative entropy of activation. Alternatively, one can argue that for compounds having relatively low coalescence temperatures, the systematic error for the determination of the enthalpy and entropy of activation is much greater than for compounds having high coalescence temperatures. This is, however, not borne out from the experiments of Oki *et al*[14] on 5,7-dihydrobenzo-[c,e] thiepins having low coalescence temperatures.

iii) The temperature dependence of $\Delta G^{\neq}$ also presents some inconsistency between the two series of compounds. Thus while for the non-methoxylated compounds (II), (III) and (VI), the $\Delta G^{\neq}$ values at T_c, 100° and 180° are fairly constant, for the methoxylated compounds (I), (IV) and (VII), the ΔG^{*} values vary appreciably with temperature. This is, of course, expected from the difference in the entropy of activation in the two series Comparison of the $\Delta G_c^{\ddagger}$ values at coalescence temperatures, therefore, may not be a true index of the relative restricted rotation in this series. The values are to be taken qualitatively rather than quantitatively

Three 1-aryl-1,4-dihydro-4,4,6-trimethyl-2-thiopyrimidones (XIII)-(XV) were studied by dynamic nmr technique. The two rings connected by a C-N bond are dissymmetrically substituted and so if the rotation about this bond is sufficiently restricted by *ortho*-substitution in the phenyl ring, the two geminal methyl groups at C-4 might be chemically nonequivalent and would appear as a doublet. This happens to be the case for compounds (XIII) and (XV), the two 4-methyl groups giving two signals around δ 1 40 with small $\Delta\nu$ values (1 5-3 0 Hz) depending to some extent on the solvents used (see Table 2) In these two cases, the inversion rate, k_c, at T_c was determined by equation (6)[18] and then the free energy of activation was obtained by substituting the value of k_c in equation (2) The $\Delta G_c^{\ddagger}$ values range between 97.90 and 100 24 kJ mol^{-1} which are little higher than the energy barriers to rotation about C-N bond in 1-arylhydantoins[20] and N-arylsuccinimides[21] in which six-membered thiopyrimidone ring is replaced by similarly constituted five-membered one.

$$k_c = \frac{\pi \Delta\nu}{\sqrt{2}} \qquad \text{.. (6)}$$

The almost equal values of $\Delta G_c^{\ddagger}$ for the compounds (XIII) and (XV), inspite of the fact that nitro group is much bulkier than methoxyl, is certainly due to resonance stabilisation of the transition state in the latter. Since the chemical shift difference is very small, the line shape analysis by taking the spectra at different temperatures would not have helped much. In the case of *o*-methyl compound (XIV) and of a few more similar compounds[7], the differential aromatic ring anisotropy is not strong enough to cause any chemical shift difference in the geminal methyl groups situated at the other end of the molecule.

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Polymerization of Methacrylamide Initiated by Ceric Ion-Malic Acid Redox System

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The homogeneous polymerization of methacrylamide (M) was studied in aqueous sulphuric acid medium at $35 \pm 0.2°$ under a nitrogen atmosphere. The rate of monomer disappearance was proportional to $[MA]^1[Ce(IV)]^1[M]^{1.5}$ and the rate of ceric ion disappearance was directly proportional to [Ce(IV)] but independent of [M]. The rate increased very slowly upto a certain range of malic acid (MA) concentration above which it remained constant. A very stable complex was revealed by Lineweaver-Burk plot of $rate^{-1}$ vs $[MA]^{-1}$. Increasing reaction temperature increased the rate from 25 to 45°. The activation energy was found to be 15.25 k cal mol^{-1}. By decreasing *pH* of the medium the rate of polymerization decreased

SEVERAL papers have appeared on the polymerization of acrylamide initiated by various redox systems[1-3]. However, the polymerization of methacrylamide has not been attended to so much. Misra *et al* have investigated the polymerization of methacrylamide initiated by persulphate-thiomalic acid[4] and persulphate-ascorbic acid[5] redox systems. Burfield and Ng[6] studied the polymerization of methacrylamide initiated by persulphate alone. The present investigation has been carried out with a view to throw light on the mechanism of polymerization of methacrylamide.

Experimental

Methacrylamide (E. Merck) was purified by two recrystalizations from acetone and dried under vacuum over calcium chloride. Malic acid (Reidal), ceric ammonium sulphate (Loba Chemie) and sulphuric acid (all AR or equivalent grade) were used as such. Double distilled water was used as solvent in all the experiments. The polymerization apparatus and procedure adopted was similar to that used by Misra *et al*[5]. The ceric ion concentration in the reaction system was determined by ceremetry. The reaction mixture was quenched by the addition of excess of standard ferrous ammonium sulphate and the excess of Fe(II) was determined by titrating it against standard ceric solution using ferroin as indicator.

Results and Discussion

Rate of monomer disappearance :

Malic acid dependence : The initial rate and maximum conversion increased with increasing [MA] from 11.25×10^{-3} to 72.00×10^{-3} mol/l at constant [M], [Ce(IV)] and $[H_2SO_4]$. However, below 6.00×10^{-3} mol/l of [MA] the polymerization was negligibly small. At lower [MA] the production of primary radicals is very low, hence initial rate and maximum conversion are at the lowest. As [MA] increases the production of primary free radicals by interactions with ceric ion increases and hence initial rate and maximum conversion also

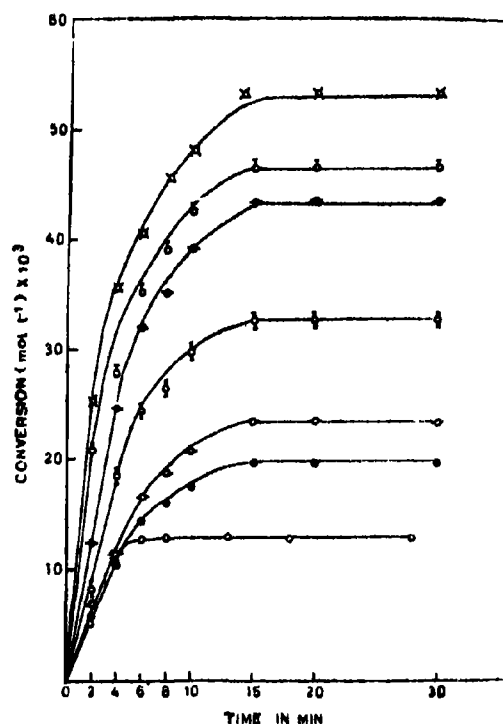



Fig 1. Polymerization of methacrylamide with varying initial concentrations of malic acid at constant [M] = 0.044 mol/l ; [Ce(IV)] = 0.002 mol/l, $[H_2SO_4]$ = 0.125 mol/l ; Temp. $35 \pm 0.2°$.

increase (Fig. 1). The malic acid exponent was found to be unity which indicated a unimolecular termination mechanism.

Ceric ion dependence: The initial rate and maximum conversion increased with increasing ceric ion concentration from 2.5×10^{-4} to 50×10^{-4} mol/l at fixed [M], [MA] and [H_2SO_4]. However, above 50×10^{-4} mol/l concentration of ceric ion the initial rate and maximum conversion decreased. At any fixed [MA] an increase in [Ce(IV)] increases the rate of production of active free radicals from malic acid by oxidation, hence rate and maximum conversion increased. Above 50×10^{-4} mol/l of [Ce(IV)] the initial rate decreased showing that at higher [Ce(IV)] the metal ion may get involved in termination reaction as well. The ceric ion exponent of unity confirmed the unimolecular termination mechanism. Several workers have reported the unimolecular termination mechanism[3,7,8]. Dainton proposed that the unimolecular termination mechanism of growing chains in aqueous phase is due to the dissolved metal ions. On the other hand Palit and Konar[9] suggested that unimolecular chain termination in heterogenous media may be due to degradative chain transfer, or by dissolved metal ions or by the occlusion of the growing radicals in the cage of polymer coils.

Monomer dependence: Increasing [M] from 7.03×10^{-2} to 42.19×10^{-2} mol/l increased the initial rate and maximum conversion at fixed [MA], [Ce(IV)] and [H_2SO_4]. The more the concentration of monomer the more are the chances of initiation, higher the propagation magnitude and hence higher the initial rate and maximum conversion. The monomer exponent of near unity (1.2) rules out the possibility of primary radical termination. The samples of the polymethacrylamide formed became insoluble due to which the degree of polymerization could not be determined. The insolubility of the polymer samples is probably due to the intermolecular imidization or due to crosslinking in the polymer chains.

Temperature dependence: The effect of temperature on the rate was studied within the range 25 to 45°. As the temperature increases the initial rate and maximum conversion increased which is due to the increased frequency of initiation that enhances the rate and maximum conversion. The activation energy was found to be 15.25 k cal mol^{-1}.

Sulphuric acid dependence: Increasing sulphuric acid concentration decreased the rate of polymerization at fixed [M], [MA] and [Ce(IV)]. This is possibly due to the formation of a highly sulphated complex of ceric ion that predominates at higher [H_2SO_4]. This highly sulphated complex of ceric ion has been suggested to be less reactive[10]. This was also proved in our laboratory by carrying out reactions with ceric ion in aqueous and sulphuric acid solutions. The rate in case of freshly prepared aqueous solutions of ceric ion are always higher than the rates observed in case of same concentration of ceric ion in sulphuric acid. By postulating $Ce(SO_4)_2$ to be the reactive species it is evident that as [H_2SO_4] is increased the HSO_4^- ions produced will compete with the malic acid molecules by acting as ligands, and hence initial rate and maximum conversion should decrease. Further, it is known that ceric ion associates successively with one, two, three and four sulphate ions to form complexes which render the ceric ion almost inactive.

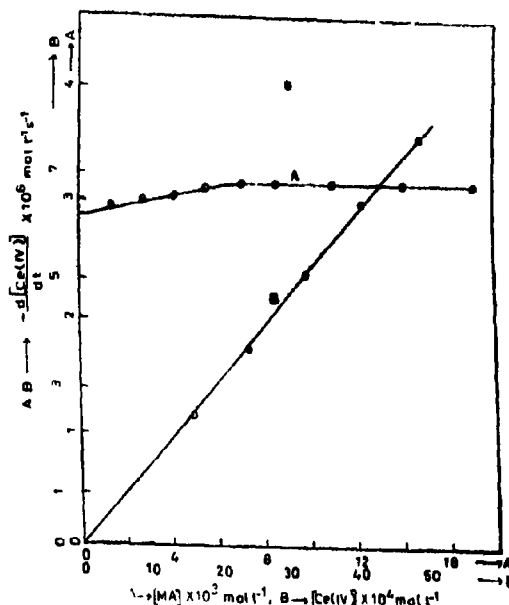



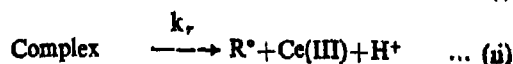
Fig. 2 Plot of $-\frac{d[Ce(IV)]}{dt}\times10^{6}$ mol/l/s vs (A)-[MA], (B)-[Ce(IV)]

For (A): [M] $=7.03\times10^{-2}$ mol/l, [Ce(IV)] 2.05×10^{-3} mol/l; [H_2SO_4] $=6.83\times10^{-2}$ mol/l; Temp. 35±0.2°.

For (B): [M] $=4.22\times10^{-2}$ mol/l; [MA] $=11.06\times10^{-3}$ mol/l, [H_2SO_4] $=16.39\times10^{-2}$ mol/l; Temp. 35±0.2°

Rate of ceric ion disappearance: The rate of ceric ion disappearance increased with increasing [Ce(IV)]. Plot of rate vs [Ce(IV)] gave a straight line passing through the origin (Fig. 2B). The rate was found to be independent of [M]. Both these observations suggest that ceric ion participates only in the redox reaction but not in initiation or termination reactions. The rate increased slightly with increasing [MA] upto a certain range above which it remained constant (Fig. 2A). This shows a strong complex formation between ceric ion and malic acid in the reaction system that decomposes in presence of sulphuric acid to give free radicals ($R^\bullet$).

$$Ce(IV)+MA \xrightarrow{K} Complex \quad \ldots (i)$$

$$Complex \xrightarrow{k_r} R^\bullet+Ce(III)+H^+ \quad \ldots (ii)$$

where K and k_r are the formation and decomposition constants of the complex. The complex formation was confirmed by Lineweaver-Burk plot of $rate^{-1}$ vs $[MA]^{-1}$ which left a considerable intercept

on the ordinate. *p*H studies revealed a 1 : 1 complex formation between ceric ion and malic acid. The ir spectra of the complex gave a peak at 1550 cm^{-1} (a shift). No peak appeared at 1725 cm^{-1} which was observed in malic acid spectrum. This shift in the peak and a peak at 560 cm^{-1} show the possible presence of metal-oxygen bonding in the complex.

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Formylcamphor Condensed with Diamines : The Structure in Solution as Obtained from UV Absorption and Circular Dichroism Spectroscopy

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The condensation products of the stereoisomers of 1,2-diamino-1,2-diphenylethane with two molecules of formylcamphor have been investigated by means of uv absorption and circular dichroism spectroscopy. In chloroform such compounds take on a *syn* configuration with hydrogen bonding within an α-(N-alkylaminoethylene) camphor group, and the intense $\pi\rightarrow\pi^*$ transitions of the chromophore will couple in dimers provided the chromophores are near to each other It is demonstrated how information about the relative orientation of the two formylcamphor groups may be obtained using the signs and envelopes of the $\pi\rightarrow\pi^*$ transition bands.

SCHIFF base condensation products of formylcamphor and various 1,2-diamines have been rather thoroughly investigated and quite different conclusions have been reached concerning the stereochemistry of these compounds in various solvents[1-3].

With the purpose of studying further the rotational conformations around substituted ethylene bridges showing that the stereochemistry of these rather complicated compounds can be understood within an exciton formalism, the condensation products between formylcamphor and the stereoisomers of 1,2-diamino-1,2-diphenylethane (stilbenediamine) have been investigated.

It has been the conclusion of previous papers in this subject[1,3] that minimum potential energy even for closely related molecules can be achieved in quite different ways e.g. in R-chxn(fmcH)$_2$ and S-chxn(fmcH)$_2$ the rigidity of the cyclohexane ring is a dominating factor which forces the two diastereoisomers to take Δ and Λ configurations, respectively. The configuration[4] is given in terms of handedness of the pair of lines connecting N and O of each aminomethylenecamphor group, and thus simultaneously representing the $\pi\rightarrow\pi^*$ transition dipole moment of the chromophores.

In contrast to this it was shown that when the barrier towards rotation around the C-C bond of the diamine is low, the stereochemistry of the compounds is determined by the asymmetric bulkiness of the camphor skeleton as e.g. R-pn(fmcH)$_2$ and S-pn(fmcH)$_2$ have the same absolute configuration of the above mentioned pair of lines (Δ)[1,3].

Finally, it was demonstrated that *meso* compounds, e.g. R,S-chxn(fmcH)$_2$ and R,S-2,3-bn-(fmcH)$_2$, exhibit co-existence of the two possible forms (*e,a*) and (*a,e*) and that equivalence exists in the behaviour between *meso* compounds and compounds with an optically inactive ethylene bridge, e.g, en(fmcH)$_2$ and ibn(fmcH)$_2$[3]; spectra of the latter compound have not been published earlier, but are quite analogous to those of en(fmcH)$_2$. Therefore at room temperature and in aged chloroform solutions two *gauche* rotamers of the ethylene bridge exist in equilibrium with the *trans* form. The equilibrium, however, may be displaced at lower temperatures, and judged from the CD spectrum of ibn(fmcH)$_2$ in $CHCl_3$ at —60° (compare Table 2 of Ref 1) this should be towards the opposite absolute configuration of R-chxn(fmcH)$_2$. A consequence of the difference in configuration between R-pn(fmcH)$_2$ and S-pn(fmcH)$_2$ on one hand and the *meso* and optically inactive compounds on the other is that, although it looks that the camphor groups are the stereochemically determining factors as soon as the rotation around the ethylene bridge is reasonably free, asymmetric methyl groups on the ethylene bridge are also involved in defining the minimum potential energy. Certainly, it is demonstrated from the above argumentation that formylcamphor Schiff base condensates with 1,2-diamines are compounds where the different substituents are heavily embedded into each other.

Experimental

Racemic stilbenediamine was prepared and resolved according to Williams and Bailar[5] and Ugo *et al*[5], respectively, *meso*-stilbenediamine was prepared according to Irving and Parkins[6], and formylcamphor was prepared from natural $(+)_D$-camphor according to Bishop *et al*[7]. The identity of the compounds was established through chemical analyses.

Assignments of absolute configuration of optical active diamines have been done according to Gillard[8].

Ultraviolet absorption spectra were measured with a Cary 14 spectrophotometer and circular dichroism spectra with a Roussel-Jouan dicrograph II.
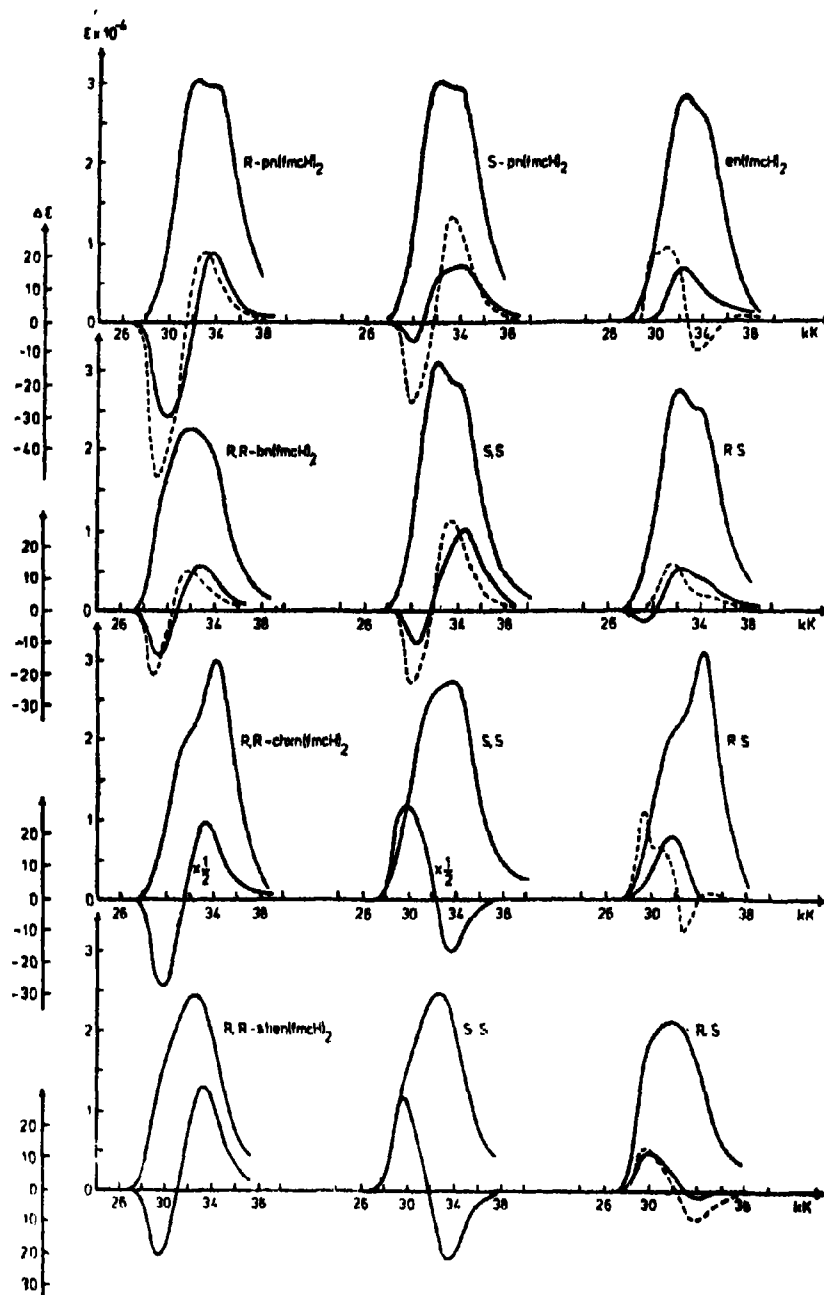
Fig 1. Molar absorptions and circular dichroisms of various condensates dissolved and aged in $CHCl_3$. Full lines ; room temperatures ; Broken lines ; $-60°$. In cases with broken lines in the CD-spectra no changes occur with temperature. All dipole strengths are $\sim 2.10^{-39}$ cm^3 cm^{-1}.

Abbreviations :

R-stien = $(+)_D$-(R,R)-1,2-diamino-1,2-diphenylethane

S-stien = $(-)_D$-(S,S)-1,2-diamino-1,2-diphenylethane

R,S-stien = *meso*-(R,S)-1,2-diamino-1,2-diphenylethane

R-chxn = $(-)_D$-*trans*-(R,R)-1,2-cyclohexanediamine

S-chxn = $(+)_D$-*trans*-(S,S)-1,2-cyclohexanediamine

R,S-chxn = *meso*-(R,S)-1,2-cyclohexanediamine

R-2,3-bn = $(-)_D$-(R,R)-2,3-butanediamine

S-2,3-bn = $(+)_D$-(S,S)-2,3-butanediamine

R,S-2,3-bn = *meso*-(*R*,*S*)-2,3-butanediamine
R-pn = $(-)_D$-(*R*)-1,2-propanediamine
S-pn = $(+)_D$-(*S*)-1,2-propanediamine
en = 1,2-ethanediamine
ibn = 2-methyl-1,2-propanediamine
fmcH = formylcamphor

R-pn$(fmcH)_2$ etc. symbolize the "Schiff base" condensates formed from one molecule of diamine and two molecules of diketones

Results and Discussion

The Schiff base condensates of stilbenediamine and formylcamphor show the same kind of *syn/anti* tautomerisation depending on the ability of the solvent to form hydrogen bonds, as was demonstrated earlier for similar compounds[1], and accordingly we will, in what follows, only refer to the spectra of aged chloroform solutions. In such solution it is possible by ^1H nmr spectroscopy to confirm that the *syn* configuration of the chromophore is the dominating species. The reason why we wish to be certain that we work with the *syn* configuration is that we want to discuss spectral behaviour in an exciton formalism with reference to the acetylacetone chromophore[9], which independent of solvent is found in a *syn* configuration.

The spectra of R-stien$(fmcH)_2$, S-stien$(fmcH)_2$ and R,S-stien$(fmcH)_2$ are given in Fig. 1.

The spectra are measured approximately 2 hr after dissolution, at which time *syn/anti* ratio from nmr is estimated to ~10/1. Prolonged dissolution in $CHCl_3$ seems to accelerate a destruction as the $\pi \rightarrow \pi^*$ transition intensity falls off markedly after 5 hr. The destruction products have not been investigated.

If one considers absorption and circular dichroism spectra of the two diastereoisomers R- and S-stien$(fmcH)_2$, it is seen that these fit nicely with expectations based on the order pn<2,3-bn<stien with respect to increasing barrier towards rotation around the substituted ethylene bridge. This is to say that while R- and S-pn$(fmcH)_2$, and R- and S-2,3-bn$(fmcH)_2$ choose the same absolute configuration of the diastereoisomers, this is not the case with R- and S-stien$(fmcH)_2$ which has a mirror image relationship. A mirror image relationship was also seen with R- and S-chxn$(fmcH)_2$[1], and in that case was a consequence of an infinitely great barrier towards rotation around the substituted ethylene bridge. Cooling to −60° does not accentuate the CD-spectra very much and although the absorption spectra do not show a marked exciton splitting there cannot be very much *trans* rotamer present in solution, because of the magnitudes of the Cotton effects

Turning our attention towards the spectral behaviour of R,S-stien$(fmcH)_2$, it is seen that the exciton splitting in the absorption band is even less marked than with the active compounds discussed. This means that the distribution between the *gauche* and *trans* rotamers at room temperature is probably placed rather much towards the *trans* form. This conclusion is confirmed by the CD spectrum which is not characteristic of exciton coupling at room temperature, whereas cooling enforces such a behaviour, thereby meaning that this species like the rest of the investigated *meso* and optically inactive diamine condensates with formylcamphor, has the Λ configuration of the chromophores as the low energy one. This set of information supports the conclusion that asymmetric substituents on the ethylene bridge in the condensates of formylcamphor and 1,2-diamines do not directly determine but do influence seriously the way in which minimum potential energy is achieved.

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Thermodynamics of Ferrous-1,10-Phenanthroline in *t*-Butanol-Water and Glycerol-Water Media at 25°

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The enthalpies of formation of ferrous-1,10-phenanthroline in *t*-BuOH-water and glycerol-water mixtures at 25° have been determined by calorimetry. The stability constants of the complex in the above mixed solvents have been determined spectrophotometrically. The entropy-changes have been evaluated combining the enthalpy values with the corresponding free energy changes calculated from *p*K values. The role of solvents on the thermodynamic parameters has been discussed.

1,10-Phenanthroline and its Fe(II) complex are well known for their use in analytical chemistry and also in view of their possible use as corrosion-inhibitors in boilers[1]. Since the first determination of the stability constants of phenanthrolinium ion and its ferrous complex by Dwyer and Nyholm[2], different workers[3-11] have studied these systems. Lahiri and Aditya[12] made a detailed spectrophotometric study and reported on the thermodynamic properties of phenanthrolinium ion, ferroin and ferriin in aqueous medium. The dissociation constants as well as the enthalpies of the reactions in methanol-water medium were studied in this laboratory by Biswas and Aditya[13]. We also presented in an earlier communication[14] the thermodynamics of 2,2'-dipyridinium ion and 1,10-phenanthrolinium ion in *t*-butanol-water and glycerol-water media at 25°. In this communication we report the enthalpies of formation of $FePh_3^{2+}$ in different *t*-butanol- and glycerol-water mixtures at 25° determined by calorimetry and the dissociation constants by spectrophotometry. $\Delta G°$ and $\Delta S°$ values were calculated from these experimental results.

Experimental

The solutions were prepared as reported earlier[14,15]. Purification of solvents was described in an earlier communication[16].

For the measurement of enthalpy change we used a microcalorimeter fabricated in this laboratory[17,18]. Experimental determinations were carried out in the same way as described in the case of $Fedipy_3^{2+}$ reported earlier[15]. In the present case also we note that the addition of a small volume of Mohr solution to a large excess of 1,10-phenanthroline gives a constant value of ΔH in the *p*H-range used. The heat change due to the formation of PhH^+ ion was taken into account. For the purpose, blank experiment with no Mohr salt (5 ml of solution containing $HClO_4$ and 250 ml of Ph) was done. The concentration of Ph was always more than 30 times the concentration of Fe^{2+} ion. The stability constants of $FePh_3^{2+}$ were determined in *t*-butanol- and glycerol-water mixtures spectrophotometrically at 25° with a Beckmann DU spectrophotometer as reported in detail earlier[19].

Results and Discussion

From the measured heat liberated, enthalpy change per mole for the reaction $Fe^{2+}+3\,Ph \rightleftharpoons FePh_3^{2+}$ was calculated, using the relation $\Delta H = -\frac{Q}{x}$, where Q represents the heat liberated in Joules for x moles of $FePh_3^{2+}$ formed. The reaction is iso-electric and as such ionic strength has very little effect. So the experimentally determined ΔHs have been taken as $\Delta H°$s. The dissociation constants and the $\Delta H°$s for $FePh_3^{2+} \rightleftharpoons Fe^{2+}+3Ph$, in *t*-butanol- and glycerol-water have been presented in columns 2 and 3 of Table 2 and in columns 6 and 7 of Table 3, respectively.

TABLE 1—THERMODYNAMICS OF $FePh_3^{2+}$ IN AQUEOUS MEDIUM AT 25°

Reaction	$\Delta G°$ (kJ mole^{-1})	$\Delta H°$ (kJ mole^{-1})	$\Delta S°$ (kJ mole^{-1})
	116.90	131.04[a]	47.28
$FePh_3^{2+} \rightleftharpoons Fe^{2+}+3Ph$	119.24	138.07[b]	64.43
	117.70	129.70[c]	40.27

a - Spectrophotometric value[11].
b - Calorimetric value[12].
c - Our values extrapolated from lower percentages of organic solvent.

TABLE 2—THERMODYNAMICS OF $FePh_3^{2+} \rightleftharpoons Fe^{2+}+3Ph$ IN *t*-BUTANOL AND GLYCEROL-WATER MEDIA AT 25°

Wt % of solvent	pK_{diss} Glycerol-water	pK_{diss} *t*-butanol-water
0	20.70 (±0 48)[a]	20.70 (±0.48)
10	20 52	20.20
20	20.66	19.70
30	19.70	19.10
40	19.92 (±1 10)	17.50
50	–	17.00 (±0.81)

[a] Values in parentheses indicate maximum errors.

The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $T\Delta S°$ for the above reaction in *t*-butanol- and glycerol-water have been compiled in columns

TABLE 3—THERMODYNAMICS OF $FePh_3^{2+} \rightleftharpoons Fe^{2+} + 3Ph$ IN DIFFERENT SOLVENT MEDIA AT 25°

Wt % of solvent	ΔG^o (kJ mole^{-1})				ΔH^o (kJ mole^{-1})				$T\Delta S^o$ (kJ mole^{-1})			
	Glycerol	*t*-BuOH	EtOH	MeOH	Glycerol	*t*-BuOH	EtOH	MeOH	Glycerol	*t*-BuOH	EtOH	MeOH
0	117.70	117.70	117.12	116 90	129 70	129 70	129 91	131 40	12 00	12 00	12 79	14.14
10	116.65	114 85	113.00	114.22	136 10	137 48	130 87	148 53	19 45	22 63	17.87	34 31
20	117.44	112.01	109 00	111.71	149 07	153.22	133 22	166 94	31 63	41 21	24 22	55.23
30	112.00	108.57	104.90	109 20	145.73	172 13	128 45	167 78	33 73	63 56	23.55	58.58
40	113.35	99.50	100.05	106 69	142 42	156 32	–	156 90	29 07	56.82	–	50 21
50	–	96.65	96.50	104 18	139 95	150 58	–	148 11	–	53 93	–	43 93

Values of ΔG^o at 15% and 25% for glycerol-water media are 116 10 and 114 60 kJ mole^{-1}, and for *t*-BuOH-water media are 117.90 and 109.20 kJ mole^{-1}, respectively.

Values ΔH^o at 2 5% and 5% for glycerol-water media are 131 00 ($\pm$0.02) and 132 67 ($\pm$0.04) kJ mole^{-1} and for *t*-BuOH-water media are 131.54 ($\pm$0.03) and 133.51 ($\pm$0 04) kJ mole^{-1}, respectively.

2, 3, 6, 7, 10, 11 of Table 3 along with the same in EtOH-[17,20] and MeOH-water[18] (reported earlier) in columns 4, 5, 8, 9, 12, 13 of the same table. The Figs. 1, 2 and 3 indicate the nature of the plots of ΔH^o, ΔG^o and $T\Delta S^o$ against wt %, mole-fraction of organic solvent and reciprocal of the dielectric constant of aqueo-organic solvents, respectively. The dielectric constant values necessary are taken from Conway[21] and Akerlof[22]. We have also determined the same parameters in water from the extrapolation of the ΔH^o and ΔG^o values in the region of lower percentages of organic components in water. The values of the thermodynamic parameters of $FePh_3^{2+}$ in water in literature along with ours are presented in Table 1. The present values are in good agreement with those of Anderegg[11] and Lahiri and Aditya[12].

In the Figs. 1 and 2 it is seen that ΔG^o changes linearly upto 30% of *t*-BuOH (which corresponds to
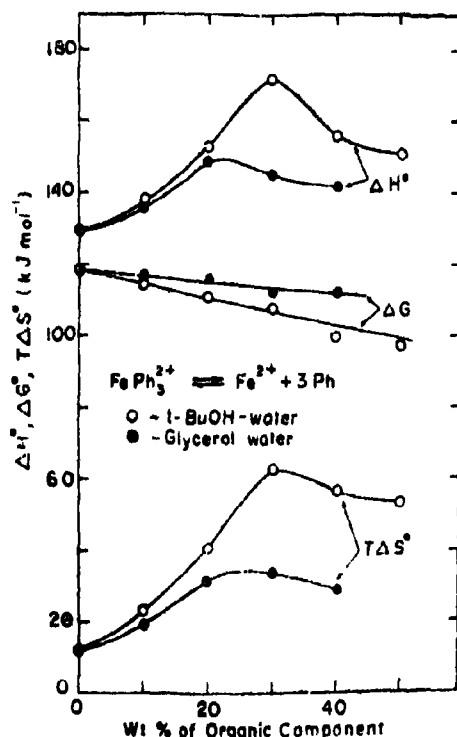
Fig. 1. Plot of ΔG^o, ΔH^o and $T\Delta S^o$ vs wt % of organic component.
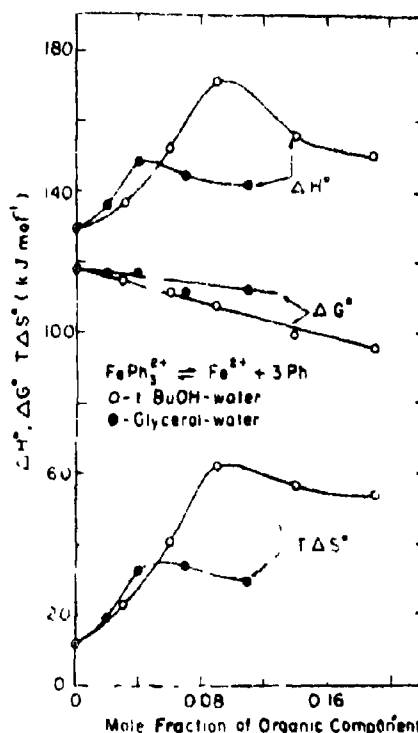
Fig. 2. Plot of ΔG^o, ΔH^o and $T\Delta S^o$ vs mole fraction of organic component

a mole-fraction of 0.09) and 20% of glycerol (corresponding to a mole-fraction of 0 04) and deviates at higher percentages. The variation of ΔH^o and $T\Delta S^o$ values with solvent composition is not linear. The values at first increase with increasing organic solvent and pass through a maximum at about 30% in case of *t*-BuOH and 20% in case of glycerol in the respective solvent mixtures. Similar behaviour has been observed by us in case of PhH^+ in *t*-BuOH- and glycerol-water mixtures[14] and also in case of $dipyH^+$ and Fe(II)-dipy complexes[15]. Such type of maximum structuration was also supported by Mishchenko *et al*[23], Krestov and Klopov[24], Pointud *et al*[25].

The interpretation of the thermodynamic data in mixed solvents is extremely difficult as it involves a knowledge of the structure of the liquid mixture and structure modification of the media when an ionic
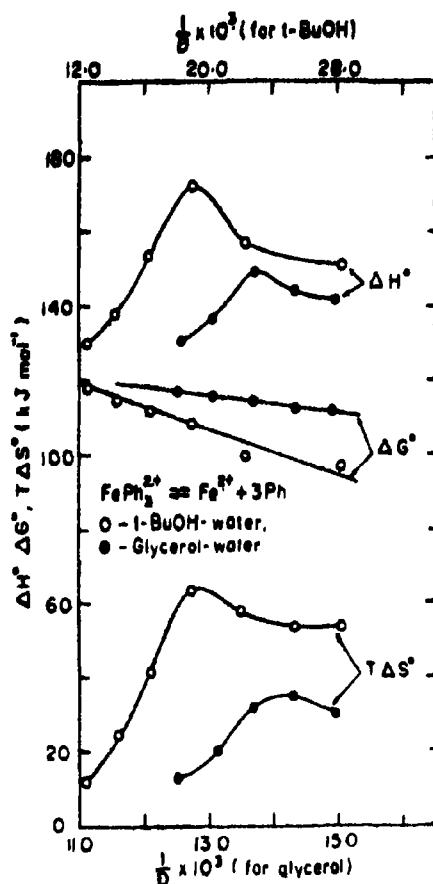
Fig. 3. Plot of $\Delta G°$, $\Delta H°$ and $T\Delta S°$ vs $1/D$ of solvent mixture (D = dielectric constant).

system is introduced in the media, in addition to ionic solvation effects.

The free energy change of transfer, $\Delta G_t^°$, which consists of electric and non-electric contributions $[\Delta G_t^° = \Delta G_{t(el)}^° + \Delta G_{t(non-el)}^°]$, in the present case will be mainly due to ion solvent and solvent-solvent interactions (non-electric part). Since the reaction is iso-electric, $\Delta G_{t(el)}^°$ will be negligible due to the small difference in the ionic ratio of $FePh_3^{2+}$ and $Fe(H_2O)_6^{2+}$ which is always solvated. $\Delta G_t^°$ indicates that the reaction is favoured in mixed solvents. This is possibly because of (i) higher solubility of Ph' in the mixed solvents, (ii) the difference in the solvational properties of $Fe(H_2O)_x^{2+}$ and $FePh_3^{2+}$ in the media, and (iii) the solvent-solvent interaction.

The entropy change of transfer of different ionic species participating in the reaction will depend on difference in entropy of the solvent media. As discussed in our earlier communication[15] for $Fe(dipy)_3^{2+}$, we have for the entropy change of $FePh_3^{2+}$

$$T\Delta S_t^° = T\Delta S_{t(Fe^{2+})} + 3T\Delta S_{t(Ph)} - T\Delta S_{t(FePh_3^{2+})}.$$

The value of $T\Delta S_t^°$ passes through a maximum based on the models by Franks and Reid[26], Kundu et al[27] and other workers[2-25].

The variation of $\Delta H°$ with solvent composition in case of $Fe(Ph)_3^{2+}$ is found to be similar to that observed in case of $Fe(dipy)_3^{2+}$. The models have been discussed in details[14,15]. The thermodynamic parameters for Fe(II)-1,10-phenanthroline complex in general vary with composition of the solvent in the same manner as the Fe(II)-dipy complex.

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Photocorrosion

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Semiconductors are often decomposed by anodic oxidation or cathodic reduction upon illumination when they are in contact with electrolytes. Examples of semiconductor corrosion are described. The mechanisms of photocorrosion for various materials are reviewed. Stabilization of semiconductor surface against photocorrosion has been discussed and the ways to prevent, to suppress, and to minimize photocorrosion are suggested. Modern analytical techniques are useful tools for future photocorrosion research.

I Electrochemical Principles of Corrosion

A. *Corrosion of metals and alloys* :

CORROSION is the interaction of a metal or alloy with its non-metallic environment. Since metals and alloys are conductors and are built up of cations and electrons that are more or less easily dissociable, and the environment usually contains ionically conducting species, most corrosion reactions are electrochemical. The stability of metals has been reviewed in detail[1].

B. *Corrosion of semiconductors* :

Semiconductors are often decomposed by anodic oxidation or cathodic reduction if they are illuminated in contact with electrolytes[2] The mechanism of these reactions has been analyzed and studied in some detail[3]. It appears that the anodic decomposition may be described as a weakening of chemical bonds at the surface of a semiconductor due to the presence of holes, that means a deficiency of electrons in bonding orbitals The cathodic decomposition may be analogously described as caused by the presence of electrons in the surface, occupying non-bonding or antibonding orbitals As a result, the weakening of the bonding of surface atoms in both cases facilitates the attack by nucleophillic or electrophillic reactants which are always present in the electrolyte.

In recent years, considerable attention had been given to the properties of semiconductors in contact with electrolytic solutions[4-6], and theories had been formulated explaining many of the results There was a critical problem of corrosion encountered with all of the materials tested, particularly the photocorrosion[2,3]. In some cases the semiconductors corrode spontaneously in the dark (forming mainly a battery), while in most instances corrosion occurs on illumination. Instead of reduced species in the aqueous electrolyte, holes in the n-type semiconductor valence band were found to oxidize the electrode itself. Holes in such an n-type semiconductor are broken bonds, while electrons in a p-type semiconductor represent excess bonds, so that in either case accumulation of the photogenerated carriers at the semiconductor surface can lead to a rupturing of the lattice. With n-type CdS, for example, the reaction on illumination is

$$CdS + 2h\nu \rightarrow Cd^{2+} + S + 2e^-$$

the two electrons can reduce Cd^{2+} at a counter electrode. The coating of elemental S covers the electrode surface in a few minutes and the reaction stops

Of course, if an electrode would remain stable under illumination, then it could be applied to generate useful chemical products in a solution, while itself only acting as a photocatalyst. Therefore, photoelectrochemical decomposition of water with semiconductors as catalysts has been extensively studied In 1972, Fujishima and Honda[7] showed that it is possible to use the semiconductor TiO_2 (rutile) in contact with water to generate both H_2 and O_2 under illumination, and claimed that the material suffered no degradation. This report soon created great enthusiasm in the field of semiconductor-electrolyte interfaces[8].

We know the corrosion phenomena, we recognize its serious problems, and we have limited knowledge about it. We are actively searching for its solutions.

II. Examples of Semiconductor Corrosion

A *Photocorrosion of TiO_2* :

Even though the TiO_2 photoanodes have been shown by many investigators to be stable, evidence indicates that they actually undergo slow dissolution in acidic solutions[9,10] Upon exposure to an 1*N* H_2SO_4 solution, the TiO_2 electrode turns velvety black in contrast to the unexposed glassy surface of the crystal. Scanning electron microscopy (SEM) reveals the presence of square tapered pits on the exposed surfaces of the crystal. This process is not a simple chemical dissolution because of its absence in the dark. Addition of 1.0 *M* $CoSO_4$ or 1.0 *M* $Co(ClO_4)_2$ to 1 *N* H_2SO_4 suppresses the anodic photodissolution of TiO_2 as evidenced by the absence of apparent changes or weight loss of the photoanode.

Some evidence of photoanodic dissolution of TiO_2 in alkaline solutions (5.0–7.0 M NaOH) at very high light intensities was also observed; a small depression in the electrode surface after about 1 hr of irradiation appeared[11].

B. *Stability of titanates* :

(a) $SrTiO_3$ electrodes, before and after the passage of electricity in the photolysis of water with 9.5 M NaOH in $H_2{}^{18}O/H_2O$, were examined by Wrighton *et al.* They concluded that the $SrTiO_3$ was stable under conditions where the electrolysis of water was photo assisted. This is the first report to show the photolysis of water without any external bias. Ohashi, McCann and Bockris[13] also found it to be stable when they combined n-$SrTiO_3$-p-CdTe and n-$SrTiO_3$-p-GaP as stable photoelectric cells.

(b) $FeTiO_3$, Fe_2TiO_4 and Fe_2TiO_5 : Iron titanate systems have been studied as possible candidates for semiconductor electrodes in PEC cells by Ginley and Baugham[14]. These authors observed the electrochemical degradation of the titanates with leaching of iron out of the surface. This poses a serious problem in spite of the reasonable chemical stability of these materials.

(c) $BaTiO_3$: Photolysis of water using $BaTiO_3$ electrodes has been studied by Nasby and Quinn[15]. No apparent electrode degradation has been observed for solutions in the pH range 1.1 to 13.6

C. *Acid dissolution of* Fe_2O_3 :

The possibility of using Fe_2O_3 as semiconductor electrodes in photoelectrochemical cells has been investigated. Hardee and Bond[16] observed gas evolution with the anodic current which they attribute to the photo assisted oxidation of water to produce O_2. They found that the potential for the onset of the photocurrent shifts to more negative values with increasing pH of the solution. The Fe_2O_3 films are seen to be stable at open circuit in basic solutions up to 1 M NaOH On the other hand, acid solutions (pH$<$4.5) slowly dissolve the Fe_2O_3 coating[17].

The acid dissolution of Fe_2O_3 seems to be not related to photocorrosion. It may be simply the increasing solubility of Fe_2O_3 in an acidic solution.

But Yeh and Hackerman[18] reported no noticeable corrosion problems with Fe_2O_3 in pH 4.0 acetate buffer to 5 5 M KOH solutions.

D. SnO_2 :

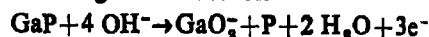
Photo effects at polycrystalline SnO_2 electrodes have been demonstrated by Kim and Laitinen[19]. The photo assisted electrolysis of water by uv irradation of a Sb-doped SnO_2 electrode has been studied by Wrighton[20]. In acidic or weakly alkaline solutions, small amounts of H_2O_2 are also formed[12].

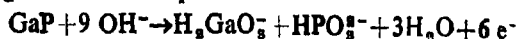
E. *ZnO and* Cu_2O :

Gerischer[21] states that the reduction of ZnO can occur at high cathodic polarization where the surface degenerates. Thermodynamic considerations by Gerscher[21] also show that the cathodic and anodic decomposition potentials are close together and both are far inside the band gap of the Cu_2O. This system is therefore very unstable and unsuitable as a photo electrode in a PEC cell.

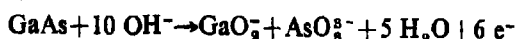
F. *GaP, GaAs, CdTe, CdS, ZnSe and ZnTe* :

According to Memming and Schwandt[22], irradiation of an n-GaP electrode in alkaline solutions yields electron flow from GaP to the counter electrode, resulting in photoanodic dissolution of GaP according to the reaction

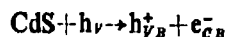
$$GaP+4\,OH^- \rightarrow GaO_2^- + P + 2\,H_2O + 3e^-$$

At higher current densities (10 mA/cm^2), the following reaction takes place[22]

$$GaP+9\,OH^- \rightarrow H_2GaO_3^- + HPO_3^{2-} + 3H_2O + 6\,e^-$$

In acidic solutions, these studies have shown that Ga and P are dissolved in the trivalent and pentavalent states, respectively with the consumption of 6 positive holes.

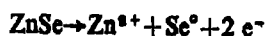
Analytical studies of the photoanodic dissolution of GaAs have been reported[24]. In alkaline solutions, GaAs dissolution takes place according to the reaction

$$GaAs+10\,OH^- \rightarrow GaO_2^- + AsO_3^{3-} + 5\,H_2O + 6\,e^-$$

The photoanodic dissolution of CdS electrodes has been described[9,25] according to the reactions

$$CdS + h\nu \rightarrow h^+_{VB} + e^-_{CB}$$

$$2\,h^+_{VB} + CdS \rightarrow S_{ad} + Cd^{2+}$$

Despite of anodic dissolution of CdTe, the combinations of n-TiO_2 and n-$SrTiO_3$ with p-CdTe and p-GaP have been reported to form separate, stable self-driven PEC cells[13]. Ohashi *et al*[26] have investigated ZnTe and CdTe as possible candidates for photo cathodes in PEC cells Their studies show that CdTe can be used as stable photocathode in a PEC cell consisting of CdTe/NaOH/TiO_2 but ZnTe is unstable and has unfavourable photo response characteristics.

The photodecomposition of ZnSe illustrates a common property of binary compound semiconductors[45]. Very stable semiconductors decompose rapidly in an electrolyte solution on illumination When an electrode of conducting n-type ZnSe and a piece of Pt wire are immersed in an inert aqueous electrolyte solution and the external leads are short-circuited, nothing happens in the dark. However, if the electrode is illuminated, a remarkably efficient reaction starts. The ZnSe has a band gap of 2.7 eV and is normally pale yellow in colour. After a few minutes of irradiation, its surface turns dark red due to the oxidation of Se^{2-} to Se°. Analysis of the solution also shows the dissolution of Zn^{2+} ion. Two electrons pass through the external circuit from the ZnSe electrode to the Pt electrode according to the overall reaction

$$ZnSe \rightarrow Zn^{2+} + Se^{\circ} + 2\,e^-$$

To understand the relation between the conductivity type and the chemical reaction rate, we may consider that in an ionic compound, the conduction band can be associated with the cations and the valence band with the anions. This may be partially

valid for partially ionic compounds such as ZnSe. Based on the relative thermodynamic properties of the ions, there is a tendency towards a symmetric dissolution. A Zn^{2+} ion in the crystal goes into solution, leaving behind two negative charges on a Se^{2-} ion that remains bound to the solid. For electrostatic reasons, the dissolution soon ceases unless the negative charges on the Se^{2-} can move out of the crystal passing through the external circuit. This is difficult in an n-type semiconductor. In order to move charges out of the crystal it must get to the conduction band, because this is where charge moves in an n-type semiconductor. For getting to the conduction band, it requires 2.7 eV excitation energy which cannot be supplied by thermal excitation at room temperature. As a result, there is no decomposition in the dark. On illumination, holes become available. These flow to the surface and so neutralize the negative charges. At the same time the electrons excited by the radiation flow in the opposite direction through the conduction band and into the external circuit to complete the charge balance. The dissolution of ZnSe crystal continues until it is blocked by the coating of a layer of slightly soluble material on its surface. Theoretically, if the ZnSe had been p-type, the charge neutralization required for the dissolution could have been supplied by the flow of thermally excited holes through the valence band. The dark dissolution should take place. No experiment with the p-type ZnSe was reported[48].

G. *WO_3* :

WO_3 shows no weight changes after prolonged passage of electricity under strong irradiation.

H. *Si* :

Another kind of reaction that consumes the electrode material is the anodic oxidation of covalent semiconductors requiring a supply of holes to the surface[48]. An important example that requires a supply of holes is the anodic oxidation of Si. For an n-type crystal there is a Schottky barrier at its surface with the usual reactifying i-V behaviour. The overall reaction is

$$Si + 2\,H_2O + zP^+ \rightarrow SiO_2 + 4\,H^+ + (4+z)\,e^-\,,$$

the experimentally obtained values for z vary from 2 to 4 depending on the reaction conditions.

III. Stabilization of Semiconductor Surface against Photocorrosion

Recently, impressive progress has been made in the development of photoelectrochemical solar cells. However, a major difficulty remains, that is, the photocorrosion of desirable anode materials such as GaAs and n-Si. Ultimately, the goal is to make photoelectric cells using polycrystalline materials[37,44], which will contain different defects. Simple theory suggests that defective areas of the crystal surface will be more difficult to stabilize[38]. Experimentally speaking, it is unclear what effects these defects will have on the photoelectrochemical corrosion processes.

A great number of efforts have been made in the past to prevent, to surpress, or to minimize photocorrosion. These efforts may be summarized as follows.

A. *Electrode coating* :

The approach to the dissolution problem has been the use of inert coatings on the photoanode surface. Gourgand and Elliott[29] have described the use of a MoO_3 coating to prevent the electrolytic corrosion of n-GaAs under irradiation. Nakato *et al*[30] have reported the coating of a thin transparent gold film to the n-GaP surface.

Coating or deposition of a wide band-gap stable semiconductor on the surface of the unstable semiconductor has been attempted in an effort to reduce the extent of anodic photodecomposition. Tomkiewicz *et al*[31] describe the sputtering of TiO_2, SnO_2, Nb_2O_5, Al_2O_3 and Si_3N_4 on GaAs and GaAlAs. Single crystalline semiconductors, such as n-Si, p-Si, n-GaAs, p-GaAs, n-GaP, n-InP and n-CdS have been coated with n-TiO_2 resulting in unfavourable results[32]. However, Bockris and Uosaki[33] have reported the chemical vapour deposition of TiO_2 on CdS single crystals. The efficiency of this electrode is reported to be four times greater than a TiO_2 single crystal in contrast to the results of Kohl *et al*[32]. Ghosh and Maruska[34] have reported the reduced photocorrosion by the use of TiO_2 film on CdSe

In the investigation of electrocatalysis or inhibition of electrode processes of a reactant (R) at the metal electrode (M) in the presence of surface layer (S), Schultze and Habib[35] conclude that electrocatalysis and inhibition by electrosorbates and protective layers is a three-parameter problem. It depends on (a) the type of layer (ionic, covalent, neutral oxide, salt), (b) the type of reaction, and (c) the type of influence (chemical, electrostatic, geometric, etc.).

Electrodes covered with thin permeable polymer films have been studied by Doblhofer[36]. The films prepared on the anode of the glow discharge act as semi-permeable membranes. Hydrogen can be oxidized on the Pt-polymer interface of these polymer covered electrodes at rates comparable to uncovered Pt, while the films were impermeable to iron ions.

B. *Use of redox system* :

The stability problems associated with the use of CdX (X=S, Se, Te) and GaY (Y=P, As) as photoanodes in PEC cells have led some investigators to suppress anodic dissolution by the use of suitable redox systems in the electrolyte. Fe(II)-EDTA is a good stabilizing agent at *p*H 3 for n-GaAs[38].

The use of wide-gap semiconductors in PEC systems is hampered by the fact that these electrodes utilize only a small portion of the solar spectrum for efficient energy conversion. The dye sensitization approach restricts light absorption to the order of 1-2% since only monolayers of dyes are active

for electron transfer. Therefore, efforts should be made on the achievement of good stability with low band gap semiconductors like GaP, GaAs, etc. by incorporation of suitable redox couples in the electrolyte[17]. The stability of common semiconductors used as photoanodes with values of their band gap, flatbands and quantum efficiency is listed in Table 1.

TABLE 1—STABILITY OF SEMICONDUCTOR ELECTRODES FOR PHOTOCATALYTIC DECOMPOSITION OF WATER*

Material	E_{BG} eV	E_{FB} eV	Highest quantum efficiency %	Stability
TiO_2	3.0	0 05	100	Stable
$SrTiO_3$	3 2	−0.2	100	Stable
$BaTiO_3$	3 3	0.1	30	Stable
$KTaO_3$	3 5	−0.2	6	Stable
$FeTO_3$	2.2	1 1	15	Leaching of Fe noted
Fe_2TiO_4	2 2	1 2	15	Leaching of Fe notad
Fe_2TiO_5	2 2	1 5	15	Stable
Fe_2O_3	2 2	0 7	40	Stable at *p*H > 4.5
Cu_2O	2 2	–	–	Corrodes
CuO	1.7	1.0	–	Corrodes
WO_3	2 7	0 5	100	Stable in acid
ZnO	3 2	0	–	Corrodes
SnO_2	3 5	0.5	100	Stable
SiC	3.0	−1.3	–	Corrodes
V_2O_5	2.75	1.2	–	Corrodes
Si	1.1	−0.7	–	Corrodes
InP	1.3	−0 2	–	Corrodes
GaAs	1.4	−0.5	–	Corrodes
GaP	2.2	−1.0	–	p-type stable
CdS	2 4	−0.5	–	Corrodes
CdSe	1.7	−0.2	–	Corrodes
ZrO_2	5 0	−1.0	–	Stable
Cr_2O_3	1.4	–	–	Corrodes, poor response
CoO	0.5	0 8	–	Corrodes, poor response

* Abstracted from Table 1 in Ref. 9.

C. *Non-aqueous solvent system* :

The corrosion problems exhibited by so many of the small band gap semiconductors will be relieved in a non-aqueous electrolyte. For example, Kohl and Bard[37] report the photocorrosion of the semiconductors (n- and p-GaAs) electrodes in acetonitrile solutions is suppressed and does not occur until potentials were well positive of the flat band potential.

IV. Future Research of Photocorrosion

In the photoelectrochemistry, there are two challenging problems facing us, namely. (i) efficient and readily available electrode materials[38] and (ii) photocorrosion. For the long range research on photocorrosion the following recommendations may be suggested.

A. For better theoretical understanding of the photocorrosion of materials, particularly semiconductors, to study the electrode surfaces with modern surface techniques[8,8,39].

(a) Auger electron spectroscopy (AES) has, since its inception as a commercially avilable surface chemical analytical technique, enjoyed a strong interaction with the field of material science. Corrosion is primarily concerned with the interaction of materials with their environments. AES is sensitive to all elements except H and He, and the relative sensitivities for most elements varies by only about one order of magnitude. Each element has relatively few strong Auger peaks, which limits peak overlap, and most elements do not show strong peak energy shifts, making elemental identification easy.

(b) X-ray photoelectron spectroscopy (XPS, ESCA) offers the researcher a unique capability for detecting chemical species in thin (1·2 nm) surface films, with only minor perturbation from the exciting radiation. This technique is important for the identification of corrosion imitators and for determining the nature of the first films formed in corrosion process. XPS is useful for (i) oxide-metal differentiation, (ii) differentiation of oxidation states, and (iii) identifying other chemical changes. It can provide more structural information as more is learned about its spectra of corrosion elements. The use of synergistic analytical technique such as scanning Auger microscopy, secondary ion mass spectroscopy, and ion micro probe, will provide some measure of spatial definition when combined with XPS.

B. To continue the current efforts to find ways to stabilize the electrodes such as coatings, doping, and combinations of electrodes[40,41]. It seems that the glow discharge polymer coating deserves more research efforts[38].

C. To stabilize the electrode surfaces with ion implantation. The ion implantation in semiconductors has been known for sometime[42]; however, little is known about its study in photocorrosion

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Spectrophotometric Study of the Reaction of Chromium(VI) with Fluphenazine Hydrochloride

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Fluphenazine hydrochloride forms a red coloured species with chromium(VI) instantaneously at room temperature in 2-5.5 *M* phosphoric acid medium. A 29-fold molar excess of the reagent is necessary for maximum development of colour intensity. The red coloured species exhibits maximum absorbance at 500 nm with molar absorptivity of 2.616×10^4 litre mol^{-1} cm^{-1}. Beer's law is valid over the concentration range of 0.05-1.85 ppm of chromium(VI). The method offers the advantages of simplicity, rapidity and sensitivity without the need for heating or extraction.

THE colour reaction between chromium(VI) and fluphenazine hydrochloride (FPH) has not been previously studied. We have now studied this coloured reaction and developed FPH as a sensitive reagent for the spectrophotometric determination of chromium(VI).

Experimental

Apparatus : Absorbance measurements were recorded with a Beckman DB spectrophotometer with matched 1 cm silica cells.

Reagents : *Chromium* (*VI*) *solution* : A stock solution of chromium(VI) was prepared from AnalaR potassium dichromate crystals in double distilled water to give a standard solution of $1 \times 10^{-2} M$. The stock solution was further diluted as needed.

FPH solution : A 0.5% (w/v) aqueous solution of FPH was prepared and stored in an amber bottle in a refrigerator.

Diverse ions : Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents.

Procedure : An aliquot of the stock solution containing 0.05-1.85 ppm of chromium(VI), 10 ml of 10 *M* phosphoric acid and 1 ml of 0.5% FPH solution were diluted to 25 ml in a volumetric flask with double distilled water, mixed well and the absorbance measured at 500 nm against a corresponding reagent blank. The amount of chromium in the sample solution was deduced from a standard calibration curve.

Results and Discussion

FPH reacts with chromium(VI) to form a red coloured species in hydrochloric, sulphuric or phosphoric acid medium at room temperature. The study of the reaction in hydrochloric or sulphuric acid medium is not recommended because the reaction is less stable and many foreign ions interfere in the determination of chromium(VI). Hence, phosphoric acid medium has been selected.

The maximum colour intensity is observed in 2-5.5 *M* phosphoric acid. Below and above this acid range the absorbance is not maximum. A 29-fold molar excess of the reagent is necessary for full development of colour intensity. The red coloured species, which is thought to be a radical cation[1,2], exhibits absorption maximum at 498-502 nm at which the reagent does not absorb. The absorbance readings remain constant for 45 min and are insensitive to temperature in the range 5-45° The order of addition of the reagents is not critical.

Beer's law is valid over the concentration range of 0.05-1.85 ppm of chromium(VI). The optimum concentration range evaluated by Ringbom's method[3,4] is 0.18-1.55 ppm. The sensitivity of the reaction is 1.9 ng cm^{-2} and the molar absorptivity is 2.616×10^4 litre mole^{-1}cm^{-1}.

TABLE 1—EFFECT OF DIVERSE IONS
Amount of chromium taken = 1 ppm

Ion added	Tolerance limit (ppm)	Ion added	Tolerance limit (ppm)
Fe(III)	3000	Cd(II)	2500
Co(II)	150	V(V)	0.3
Ni(II)	500	Fluoride	1100
Cu(II)	1700	Chloride	2000
Mn(II)	1500	Bromide	1300
Mo(VI)	300	Iodide	0.2
W(VI)	150	Nitrate	2000
U(VI)	200	Sulphate	1800
Pb(II)	120	Nitrite	0.3
Ca(II)	1200	Acetate	1300
Al(III)	3000	Tartrate	500
Ba(III)	5000	Oxalate	1000
Zn(II)	2000	Citrate	2200
Sr(III)	5500	EDTA	8000
Zr(IV)	150		

Effect of diverse ions : In order to assess the possible analytical applications of the method, the effect of some ions which often accompany chromium was studied by adding different amounts

of the diverse ions to 1 ppm of chromium(VI) which gave less than 2% error in absorbance readings (Table 1). The major advantage of this method is that FPH can be used as a selective reagent for the determination of chromium in presence of a large amount of iron(III).

Determination of chromium in chromium steels : Simulated samples containing chromium corresponding to chromal steel, AISI-A 4320 and AISI-ES 2100 were prepared and the chromium content was determined. There is a good agreement between the amounts of chromium taken and found.

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Spectral Studies of Polymeric Metal Complexes with Schiff Bases of Terephthalaldehyde and Hydrazides

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Polymerization reactions involving the formation of Schiff base metal complexes by condensation have been described. The Schiff bases formed are terephthalaldehyde *bis*-(benzoic acid hydrazone) (TBH) and terephthalaldehyde *bis*-(nicotinic acid hydrazone) (TNH). The ir spectra indicate that chelation occurs through their enolic form. Both hydrazones act as tetradentate ligands and a polymeric structure is proposed for 1:1 complexes. All complexes except Zn(II) are paramagnetic which along with calculated values of ligand field parameters, ν_2/ν_1, 10 Dq, B′, β and $\beta°$, obtained from electronic spectral data support an octahedral geometry.

METAL complexes[1-8] of Schiff bases of hydrazides with aldehydes and ketones have been of special interest in recent years, particularly in the context of therapeutic value of hydrazide and hydrazone. The coordination occurs both in keto[5-6] as well as enolic form[3,4] of the ligands with the metal ions. Larsen *et al*[7,8] have made an extensive study on molecular and electronic structure in metal complexes with Schiff bases of β-diketones and diamines by absorption and circular dichroism spectra. The results have been interpreted by means of molecular exciton theory to rationalize the observations on the dimeric Schiff bases. Formation of oxygen bridged bi- and trinuclear complexes have also been described in a review by Sinn and Harris[9].

The present paper describes the synthesis and characterisation of Schiff bases viz., terephthalaldehyde *bis*-(benzoic acid hydrazone) (TBH) and terephthalaldehyde *bis*-(nicotinic acid hydrazone) (TNH) and their complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The results are discussed with the aid of infrared and electronic spectra and magnetic and thermal data These complexes are similar to several coordination polymers of Schiff bases with other terephthalaldehyde derivatives, which had been initiated by Prof A. K. Dey[10-12].

Experimental

Materials :

Terephthalaldehyde (Koch Light), and nicotinic acid hydrazide and benzoic acid hydrazide were used to synthesize the Schiff bases. $Mn(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2.H_2O$, $Zn(CH_3COO)_2.2H_2O$ (all BDH. AnalaR), $Co(CH_3COO)_2.4H_2O$ (Sarabhai M.), $Ni(CH_3COO)_2.4H_2O$ (Veb Laborchemie) were used and the solvents were of reagent grade.

Preparation of Schiff bases: Benzoic acid hydrazide (13.6 g ; 0.1 mol) or nicotinic acid hydrazide (13.7 g ; 0.1 mol) and terephthalaldehyde (6.7 g ; 0.05 mol) dissolved in ethanol were mixed and refluxed on a water bath for 2 hr. The precipitated white crystalline solids were filtered, washed successively with water, ethanol, diethylether, and dried (yield *ca* 80%). The Schiff bases obtained are insoluble in water, ethanol, chloroform, benzene, acetone, toluene, xylene, but soluble in DMF and DMSO. Found : C, 72 3 ; H, 4.82 ; N, 16.05 Calcd. for $C_{22}H_{18}N_4O_2$; C, 71.35 ; H, 4.86 ; N, 15.14% and C, 64.32 ; H, 4.45 ; N, 22.94. Calcd. for $C_{20}H_{16}N_6O_2$; C, 64.51 ; H, 4.30 ; N, 22.58%.

Synthesis of Schiff base-metal complexes : TBH or TNH (0 1 mol) dissolved in DMF was gradually added to a solution of the metal salt (0.01 mol) in DMF-H_2O media. The mixture was refluxed at *ca* 120° for 2 to 3 hr as necessary and left overnight. The precipitated mass was filtered, washed with DMF, ethanol and ether and dried (yield 80-85%).

The complexes are air stable, powdery and insoluble in water and common organic solvents viz, ethanol, acetone, benzene, chloroform, nitrobenzene, THF, DMF and DMSO.

Analytical data : Microanalytical methods were used for the determination of carbon, hydrogen and nitrogen The complexes were decomposed by fuming HNO_3 and the metal contents estimated titrimetrically against EDTA.

Magnetic susceptibility : The magnetic susceptibility of the complexes were determined at 298 K by Faraday's method.

Spectral studies : IR spectra were recorded on Beckman Infrared spectrophotometer using KBr pellets in the range of 4000-400 cm^{-1}, DRS were obtained in the range 200-1000 nm using Carl-Zeiss spectrophotometer VSU-2.

Thermogravimetry : TG was done by heating the complexes upto 800° at a rate of 10° min^{-1} in air.

Results and Discussion

The analytical data of the complexes (Table 1) agree with the general formula $(ML.2H_2O)_n$ where

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M=Mn(II), Co(II), Ni(II), Cu(II), or Zn(II), L=$C_{22}H_{16}N_4O_2$ or $C_{20}H_{14}N_6O_4$.

TABLE 1—COLOUR AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	Analyses % Found (Calcd.) M	C	H	N
MnL.2H_2O	Brown	11.64 (11.97)	56.92 (57.52)	4.32 (4 35)	13 04 (12 20)
CoL.2H_2O	Reddish brown	12 26 (12.73)	57.42 (57 02)	4.30 (4.32)	12.82 (12 09)
NiL.2H_2O	Greenish yellow	12.16 (12.68)	56.96 (57.05)	4.42 (4.32)	12 69 (12.10)
CuL.2H_2O	Brown	13.05 (13.58)	56 92 (56 46)	4.35 (4.27)	12.02 (11.97)
ZnL.2H_2O	Yellow	13.21 (13.92)	56.52 (56 24)	4 48 (4.26)	12.43 (11.93)
MnL'.2H_2O	Brown	11.54 (11.91)	52.84 (52 02)	3.86 (3.90)	18.94 (18.22)
CoL'.2H_2O	Brown	12 42 (12.67)	51.48 (51.61)	3 92 (3.87)	18 76 (18 06)
NiL' 2H_2O	Yellow	12.16 (12.63)	52.04 (51 64)	3.82 (3.87)	18.99 (18.06)
CuL'.2H_2O	Brown	13.16 (13.53)	51.41 (51.11)	3.94 (3.83)	17.81 (17 88)
ZnL'.2H_2O	Yellow	13.34 (13.86)	51.02 (50.91)	3.89 (3 81)	17.95 (17.82)

L = $C_{22}H_{16}N_4O_2$, L' = $C_{20}H_{14}N_6O_4$

cteristic bands near 3250, 1650, 1300, 750 and 670 assigned to N-H stretching, C=O stretching, N-H in-plane bending, C=O in-plane deformation and C=O out-of-plane deformation, respectively[18]. The bands near 1630 and 1600 are assigned to C=N and C=C stretching, respectively. The bands at 1485 and 1050 in TNH are due to pyridine ring

TABLE 3B—IR SPECTRA* OF TNH AND ITS COMPLEXES

TNH	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Assignment
...	3500	3505	3510	3500	3510	ν OH(H_2O)
3250	.			.	..	ν NH
1655		.				ν C=O
1630	1620	1620	1615	1615	1510	ν C=N
1600	1600	1610	1600	1610	1610	ν C=C and δH_2O
	1560	1565	1560	1560	1565	ν C=N–N=C
1485	1485	1480	1485	1485	1485	ν N=N–(pyridine)
1305		...				δ NH
..	1290	1285	1285	1290	1290	ν C–O
1050	1050	1050	1045	1050	1050	ν N=N–(pyridine)
910	920	925	925	930	930	ν N–N
750	..	...	...	..	...	C=O in-plane
670			..	.	...	C=O out-of-plane deformation
	525	520	515	520	520	ν M–O
...	450	455	460	450	450	ν M–N

* Wave numbers are in cm^{-1}.

TABLE 2—MAGNETIC MOMENT, ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF TBH AND TNH* COMPLEXES

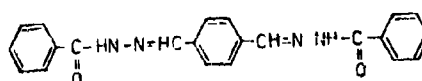
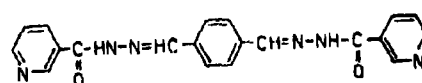
Complex with	Magnetic moment	Electronic spectra Band cm^{-1}	Assignment	ν_2/ν_1	10 Dq	B'	β	β°	Geometry
Mn(II)	5.92 (5.80)	17500	$^6A_{1g} \rightarrow T_{1g}(G)$	...	.	...	...	...	Octahedral
		21240	$\rightarrow T_{2g}(G)$						
		23450	$\rightarrow E_g(G)$						
		26520	$\rightarrow T_{2g}(D)$						
		28750	$\rightarrow E_g(D)$						
Co(II)	4.89 (4.91)	10200	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	2 1 (2.1)	11150 (11450)	893 (893)	0.919 (0 920)	800 (8.00)	Octahedral
		21350	$\rightarrow {}^4A_{2g}(F)$						
		22300	$\rightarrow {}^4T_{1g}(P)$						
Ni(II)	2.96 (3.02)	10150	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	1 5 (1.5)	10150 (10200)	922 (911)	0.873 (0 863)	12.68 (13.65)	Octahedral
		15200	$\rightarrow {}^3T_{1g}(F)$						
		27750	$\rightarrow {}^3T_{1g}(P)$						
Cu(II)	1.95 (1.98)	10100	$^2B_{1g} \rightarrow {}^2A_{1g}$		10100 (10000)		..	...	Octahedral
		11150	$\rightarrow {}^2B_{2g}$						
		15200	$\rightarrow {}^2E_g$						

* Values within the parentheses are for TNH complexes.

TABLE 3A—IR SPECTRA* OF TBH AND ITS COMPLEXES

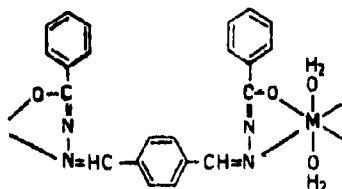
TBH	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Assignment
..	3510	3500	3510	3510	3500	ν OH(H_2O)
3250	...	...	...	...	..	ν NH
1650	...		...	..	.	ν C=O
1630	1615	1620	1620	1620	1620	ν C=N
1600	1610	1600	1600	1610	1610	δ (H_2O) + ν C=C
...	1570	1560	1560	1560	1565	ν C=N–N=C
1300		...	.	...	...	δ NH
..	1290	1290	1285	1290	1290	ν C–O
915	935	935	940	940	935	ν N–N
750	...	...	...	...	..	C=O in-plane
670	...	...	..	...	.	C=O out-of-plane deformation
.	520	520	510	510	520	ν M–O
450	450	460	460	450	455	ν M–N

* Wave numbers are in cm^{-1}.

The ir spectra (Tables 3A and 3B, wave numbers expressed in cm^{-1}) of TBH and TNH show characteristic bands near 3250, 1650, 1300, 750 and 670 assigned to N-H stretching, C=O stretching, N-H in-plane bending, C=O in-plane deformation and C=O out-of-plane deformation, respectively[18]. The bands near 1630 and 1600 are assigned to C=N and C=C stretching, respectively. The bands at 1485 and 1050 in TNH are due to pyridine ring nitrogen. All these bands in the spectra of TBH and TNH indicate that these are present in keto form, and the proposed structures I and II for the Schiff bases are as follows :

I TBH

II TNH

However, the chelation occurs through enolic form which finds support from the fact that (i) C=O stretching bands disappear and (ii) new bands

appear near 1570-50 and 1290-85 which may be assigned to C=N–N=C stretching and C–O stretching at C–O–M site, respectively. The involvement of azomethine nitrogens for coordination is indicated by (i) a negative shift in the stretching frequency of C=N group and (ii) a positive shift in the stretching vibrations of N–N group[14] in the spectra of the complexes. Coordination through oxygen and nitrogen are further supported by the occurrence of new bands at ~520-510 and ~460-450 which may be assigned to M–O and M–N stretching frequencies, respectively. The ring nitrogens in the case of TNH do not take part in coordination as the bands observed at 1485 and 1050 due to νN=N-(pyridine) remain unchanged on chelation.

Thus, both the Schiff bases act as tetradentate ligands as each metal ion is coordinated with two nitrogen and two oxygen atoms. Coordination polymerization takes place since all the four donors in one ligand molecule can not coordinate to the same metal ion due to steric factors. Two water molecules are attached to satisfy the coordination number. The presence of water molecule is indicated by the observance of strong bands at 3500 and 1600 in the ir spectra which may be assigned to νOH and δH_2O, respectively. The percentage weight loss observed between 100-200° by TG analysis correspond to the elimination of 2 H_2O, thus supporting the above assumption.

III. TBH complexes

Mn(II), Co(II), Ni(II) and Cu(II) complexes are paramagnetic and the magnetic moment values at 298 K are found to be : 5.92, 4.89, 2 96, 1.95 and 5 90, 4.91, 3 02 and 1.98 B M. for the two series of complexes, respectively. Various ligand field parameters viz., ν_2/ν_1, 10 D_q, B', β and β^* have been calculated (Table 2) from electronic spectral data. Both these data show octahedral geometry of the complexes[16-20]. The geometry, composition, insolubility and high thermal stability of the complexes indicate their polymeric nature[1,2,8,21].

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Peptide Models for the Metal-Binding Sites of Proteins and Enzymes

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A series of peptide models were utilized to probe the metal-binding sites of proteins and enzymes. Studies with three peptide analogues, GlyGly-L-His, GlyGly-L-His-$NHCH_3$ and L-Asp-L-Ala-L-His-$NHCH_3$, representing the Cu(II)-transport site of human serum albumin revealed that the Cu(II)-binding site is located at the NH_2-terminal of the protein involving the α-NH_2, imidazole, and two deprotonated peptide nitrogens and the COO^- of the Asp residue forming a pentacoordinated structure. Similarly, the investigation of the Ni(II)-transport site of human serum albumin using peptide models revealed the structure of the Ni(II)-binding site of albumin. A cyclic octapeptide, cyclo(Gly-L-Glu-Gly-Gly-L-His Gly-L-His-Gly), was designed to mimic the Zn(II)-binding site of carboxypeptidase. Structural studies with the cyclic octapeptide showed that the Zn(II) binding took place with the imidazoles of the two histidine residues and the carboxyl side chain of the glutamic acid residue, a finding similar to what is known about the Zn(II)-binding sites of carboxypeptidase Furthermore, a cyclic heptapeptide, cyclo(Gly-L-His-L-Gly-L-His-Gly-L-His-Gly), was designed to mimic the Zn(II)-binding site of carbonic anhydrase. Detailed studies with the cyclic heptapeptide showed that Zn(II) bound to this peptide involving imidazoles from all the three histidine residues as is known to be the case for the Zn(II)-binding site of carbonic anhydrase Considerations for successful design of peptide models as well as its limitations are discussed.

IMPORTANT advances have been made in recent years in the investigations of metal protein interactions in which the peptide models have played a very significant role. Small peptide molecules designed to mimic the metal binding sites of proteins and enzymes can provide valuable information which is otherwise difficult to obtain from the studies of the native molecules. Models for metal binding sites which are located on a short polypeptide chain may be designed using a linear peptide molecule with suitable side chains positioned in strategic locations. However, models to mimic the metal-binding sites originating from different parts of the polypeptide chain such as those found in most metalloenzymes and metalloproteins are difficult to design. In this case, a linear peptide may not be suitable. Cyclic peptides with side chains suitably positioned for the purpose of metal binding may provide both the rigidity and the ligand binding geometry of the native proteins and enzymes.

We have designed peptide models mimicking both types of metal-binding sites discussed above. In this article, I shall discuss some of our results with Cu(II) and Ni(II)-transport sites of human serum albumin and the Zn(II)-binding sites of two metalloenzymes: carboxypeptidase and carbonic anhydrase.

Copper(II)-transport site of human serum albumin:

Copper(II) bound to albumin is considered to be the transport form of Cu(II) in blood. It has long been known that bovine serum albumin has one strong binding site for Cu(II)[1,2]. The stoichiometry of Cu(II) binding to HSA* was established by us later[3]. The involvement of α-NH_2 at the strong Cu(II)-binding site was shown by blocking the reaction of the α-NH_2 group with 2,4-dinitrofluorobenzene by Cu(II)[4] Titrimetric studies indicated that one of the coordinating groups at the binding site had a pK_a near 8[5]. The 525 nm absorption band of the 1.1 Cu(II)-albumin complex and the displacement of two protons by the first Cu(II) at pH 9 suggested that two peptide bond nitrogens and a possible fourth coordinating atom such as an imidazole nitrogen participated along with the α-NH_2 at the strong site[6]. Subsequently, we found that dog serum albumin failed to exhibit the characteristics of a specific first binding site for Cu(II)[7]. Amino acid sequence analysis of the NH_2-terminal region of DSA showed that the third residue histidine, critical to the binding of Cu(II), has been replaced with a tyrosine residue[8]. This finding confirmed the involvement of the imidazole nitrogen in the coordination of Cu(II) in the case of HSA and BSA.

On the basis of the proposed Cu(II)-binding site of albumin involving the α-amino nitrogen, two intervening peptide nitrogens and the imidazole nitrogen of the histidine residue in the third position, three peptide analogues were designed and synthesized. The peptide glycylglycyl-L-histidine was synthesized by active ester method[9,10]. Another

*Abbreviations used: HSA, human serum albumin; BSA, bovine serum albumin; DSA, dog serum albumin; GGH, glycylglycyl-L-histidine; GGHNMA, glycylglycyl-L-histidine-N-methyl amide; AAHNMA, L-aspartyl-L-alanyl-L-histidine-N-methyl amide.

peptide analogue was prepared by derivatizing the carboxyl group to N-methyl amide to more closely resemble the protein molecule[11]. Finally, the native sequence peptide, L-aspartyl-L-alanyl-L-histidine-N-methyl amide, representing the Cu(II) transport site of HSA, was synthesized employing the N-hydroxysuccinimide ester method[12].

TABLE 1—COMPARISON OF LOG STABILITY CONSTANTS (LOG β_{pqr}, LOG β'_{pqr} and LOG β''_{pqr}) OF THE COMPLEX SPECIES $M_pH_qA_r$ [M = Cu(II), A = GLYGLY-L-HIS-N-METHYLAMIDE, A' = GLYGLY-L-HIS, A'' = L-ASP-L-ALA-L-HIS-N-METHYLAMIDE] IN 0.15 M NaCl AT 25°

p	q	r	log β_{pqr} ($M_pH_qA_r$)	log β'_{pqr} ($M_pH_qA'_r$)	log β''_{pqr} ($M_pH_qA''_r$)
0	3	1	—	17.50	17.267
0	2	1	14 47	14.78	14.286
0	1	1	8.00	8 04	7.731
1	−2	1	−0.479	−1 99	−0 55

TABLE 2—SPECTRAL PROPERTIES OF THE Cu(II)-TRANSPORT SITE OF HUMAN SERUM ALBUMIN, Cu(II)-COMPLEXES OF THE NATIVE SEQUENCE PEPTIDE, AND THE DESIGNED PEPTIDES

Cu(II) complex	λ_{max} (nm)	ϵ_{max} (liter mol^{-1} cm^{-1})
Human serum albumin-Cu(II)	525	101
GlyGly-L-His-Cu(II) ($MH_{-2}A$)	525	103
GlyGly-L-His-NHMe-Cu(II) ($MH_{-2}A$)	525	103
L-Asp-L-Ala-L-His-NHMe-Cu(II) ($MH_{-2}A$)	525	103

TABLE 3—PARAMAGNETIC RESONANCE PARAMETERS OF Cu(II) ION FOR ITS FIRST COMPLEX WITH HUMAN SERUM ALBUMIN, GLY-GLY-L-HIS-$NHCH_3$ AND L-ASP-L-ALA-L-HIS-$NHCH_3$ AT 77K

Ligand compound	pH	$g_{\parallel}$	g_m	$A_{\parallel}$ (gauss)	$A_{\parallel}^{a}$ (mk)
Human serum albumin	6.5	2 166	2 051	214	21.6
Human serum albumin	9.2	2.169	2.049	214	21.6
Gly-Gly-L-His-$NHCH_3$	6.4	2.17	2.051	211	21 3
Gly-Gly-L-His-$NHCH_3$	11.2	2.163	2.051	209	21.1
L-Asp-L-Ala-L-His-$NHCH_3$	6.5	2.167	2 050	211	21 4
L-Asp-L-Ala-L-His-$NHCH_3$	11.1	2 166	2 049	209	21 1

$^a A$ (mk) = 0 046686 g A (gauss)

The Cu(II) complex equilibria in the systems containing Cu(II) and the peptides were studied by analytical potentiometry[13,14]. The species and their stability constants are presented in Table 1. In all the systems studied, there is one major species ($MH_{-2}A$) existing in physiological pH. The spectral properties of the major Cu(II)-peptide species are almost identical to HSA-Cu(II) (Table 2). The crystal of Cu(II)-GGHNMA was prepared at physiological pH and its molecular structure was determined. It is shown in Fig. 1 that Cu(II) is tetradentately chelated by amino-terminal nitrogen, the next two peptide nitrogens and the histidyl nitrogen of a single tripeptide molecule in a slightly distorted square-planar arrangement[15]. Electron paramagnetic resonance (EPR) spectra of the synthetic peptides correspond very well with those for the Cu(II)-HSA complex[16]. The results are shown in Table 3. At 77 K, the epr spectra of Cu(II) complex of HSA exhibited only one form of epr signal between pH 6.5 and 9.5. The presence of equally spaced nine-line superhyperfine structure with spacing ~15 gauss indicated considerable covalent bonding between Cu(II) and four nitrogen atoms derived from the protein. In the pH range between 6 and 11, the epr spectra of Cu(II) complexes of AAHNMA and GGHNMA also exhibited well resolved nine-line superhyperfine structure.
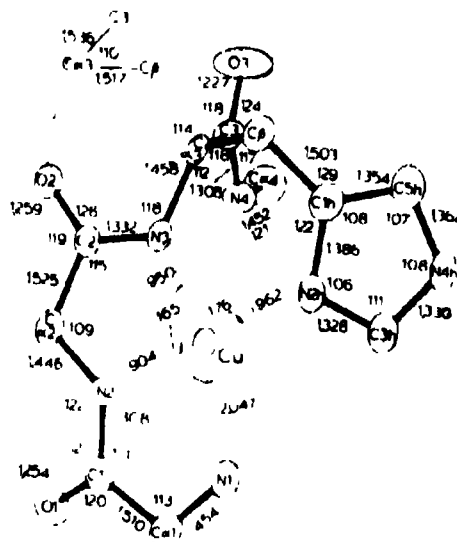
Fig. 1 Structure of the Cu(II)-complex of the designed peptide glycylglycyl-L-histidine-N-methyl amide by X-ray crystallographic analysis[15]

All the above studies showed a considerable similarity between AAHNMA and GGHNMA. However, the native sequence peptide AAHNMA resembled closer to the protein HSA as far as their Cu(II)-binding affinity and dissociation are concerned[17]. This raised the question as to whether the Cu(II)-binding site indeed involved the side chain carboxyl group in addition to the four nitrogen ligands already proposed. In order to solve this question, a detailed investigation was undertaken with ^{13}C-nmr technique[18].

The consequences of the binding of a paramagnetic metal such as Cu(II) by a ligand molecule are alterations of the chemical shifts and linewidths of the nuclear resonances of the ligand. But Cu(II) has a long electron spin relaxation time (T_s^{-1} ~ $10^8 s^{-1}$). Because of this, its dominant effect is line broadening. The broadening of line is caused by the considerable decrease of the relaxation time due to the localized magnetic field of species bearing an unpaired electron in the proximity of the nmr active nucleus. The dipolar term is usually dominant in many cases. But the scalar term which corresponds to the transfers of unpaired spin density from the metal ion to the carbon is also quite significant. If the dipolar term dominates the line broadening, the ratio of $T_1/T_2 = 7/6$. If, however, the scalar mechanism is important, $T_1/T_2 > 7/6$. In this

instance, it is possible to interpret the data in terms of actual binding of paramagnetic metal with the ligand from the line broadening results.

TABLE 4—CARBON-13 SPIN-LATTICE AND TRANSVERSE RELAXATION TIMES IN PRESENCE OF Cu(II)

[Cu(II)/peptide molar ratio 1 : 50, pH = 7.0, ω_1 = 25.16 MHz, ω_2 = 90.54 MHz].

	T_{1p}^{-1} s^{-1}	T_{2p}^{-1} s^{-1}	T_{1p}/T_{2p}	$T_{2p\,\omega_1}/T_{2p\,\omega_2}$
Asp COO^-		31		1.5
C_2	0.26	375	1440	1.6
C_4		280		1.6
C_5	0.30	230	770	1.8
Asp C_α	0.37	22	60	1.3
Asp C_β	0.40	67	170	2.3
His C_β	0.28	31	110	1.9

The observed T_1 and T_2 values for AAHNMA-Cu(II) are given in Table 4 at pH 7.0 for a Cu(II)/peptide molar ratio of 1 : 50. For all of the carbon atoms which are affected by Cu(II), the ratio $T_1/T_2 >>> 7/6$ indicates predominant scalar interactions. The lack of any frequency dependencies of the linewidth in Cu(II)-containing solution indicated that fast exchange limit was obtained in all the cases. Coordination of Cu(II) with the peptide showed a large line broadening for several ^{13}C resonances, especially C_2, C_4 and C_5 of the His, Asp C_β, Asp COO^-, and His C_β (Fig. 2). The results suggest that in addition to four nitrogen ligands (one amino, two peptide and one imidazole nitrogen) in a square-planar coordination, there is the involvement of the side chain carboxyl group forming a pentacoordinated structure (Fig. 3). Further investigation of Cu(II) interaction of the NH_2-terminal 24-residue peptide fragment of HSA by ^{13}C-nmr technique confirmed the proposed structure[19-22].

Fig 2. ^{13}C-NMR spectra (25.16 MHz) of D_2O solution containing 0.27 M L-aspartyl-L-alanyl-L-histidine-N-methyl amide and 5.41 × 10^{-3} M Cu(II). The pH of solutions was (a) 2.0, (b) 7.0 and (c) 10.0 (*corresponds to Asp COO^-)[18].

Fig 3 Structure of the Cu(II)-transport site[18].

Nickel-transport site of human serum albumin :

Nickel(II) in human serum is mainly associated with albumin and L-histidine[23]. Nickel(II), like Cu(II), blocks the reaction of 1-fluoro-2,4-dinitrobenzene with the α-amino group at the NH_2-terminus of BSA. It has also been shown in preliminary tests that increasing amounts of Ni(II) caused the characteristic purple colour of the 1 : 1 Cu(II)-BSA complex to fade and change to yellow[6]. These results suggest that Ni(II) binds at the NH_2-terminal region of albumin. Further experiments in this laboratory showed that HSA possesses a strong binding site for Ni(II)[24].

In order to investigate the nature of the Ni(II)-binding site of HSA, detailed studies were undertaken with the synthetic native sequence peptide AAHNMA. In studying the Cu(II) binding to AAHNMA, it was found that the proton-liberation
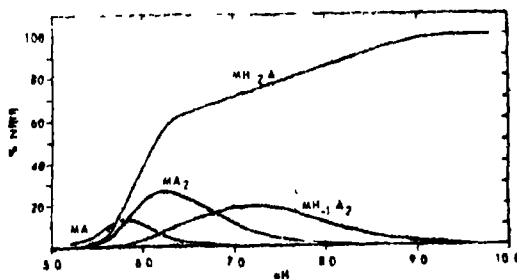
Fig 4. Species distribution for the Ni(II)-L-aspartyl-L-alanyl-L-histidine-N-methyl amide system as a function of pH. [Ni(II)] = 1.09 × $10^{-4}$$M$; [Peptide] = 4.474 × $10^{-4}$$M$. Curve 1, MA (log β_{101} = 5.50); Curve 2, MA_2 (log β_{102} = 11.56); Curve 3, $MH_{-2}A$ (log β_{1-21} = 5.94); Curve 4, $MH_{-1}A_2$ (log β_{1-12} = 4.75)[24].

reaction begins at a pH slightly above 5 and a rapid increase in $\delta H^+/\delta C_M$ occurs to a maximum of almost 3.5 at pH 6.4. This rapid displacement is attributed to the formation of the major species $MH_{-2}A$ (Fig. 4). At pH 9.5-10.0, $\delta H^+/\delta C_M$ is steady at a value of 2, where the species $MH_{-2}A$ is present exclusively. Since in this pH range the β-carboxyl, imidazole and amino groups are already titrated, the protons liberated can be attributed to complex formation by the two peptide amide groups.

The visible spectra of Ni(II) complexes of HSA and AAHNMA are very similar. Analysis of the spectra of HSA as a function of pH, in the presence of 1 equivalent of Ni(II), showed that the spectrum of hexaquo-Ni(II) with absorption maxima at 395 and at 650-720 nm (broad doublet) changes rapidly with increasing pH to a highly absorbing peak at 420 nm, indicative of a square-planar or square-pyramidal geometry about the metal ion (Fig. 5). By pH 6.9, the peak has developed well with a shoulder in the region of 450-480 nm. At higher pH, the increases in absorption are less, but a small peak develops at ?40 nm.
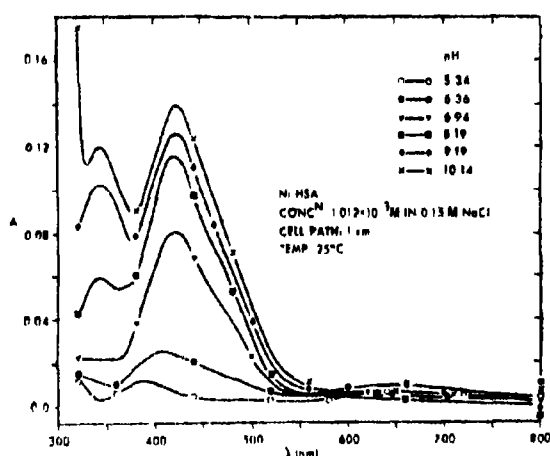
Fig 5 Visible absorption spectra as a function of pH for the Ni(II)-human serum albumin system. [Ni(II)-HSA] = 1.01 mM in 0.15M NaCl, 1 cm cell path-with protein as reference at 25°[24].

The visible absorption spectra of Ni(II)-AAHNMA are shown in Fig. 6. At pH 3.5, a spectrum of hexaquo-Ni(II) is observed. When the pH is increased to approximately 5.1, the spectrum is shifted to a λ_{max} of 385 nm and a broad peak at about 640 nm. It is possible that some initial carboxylate interaction with Ni(II) before proton liberation may be taking place, yielding a complex of octahedral symmetry. By pH 5.4, the peak maximum has shifted to 415 nm and the solution is a mixture of octahedral Ni(II) and mainly the highly absorbing MA complex (λ_{max}=428 nm, ϵ_{max}=202). As the pH is increased, the absorption at 420 nm increases sharply, coinciding with the increases in the species $MH_{-2}A$ (λ_{max} = 420, ϵ_{max}=135) as shown in the species distribution. A shoulder in the region 450-480 nm is also present on the high wavelength side of the 420 nm peak. The results are very similar to those observed with Ni(II)-HSA
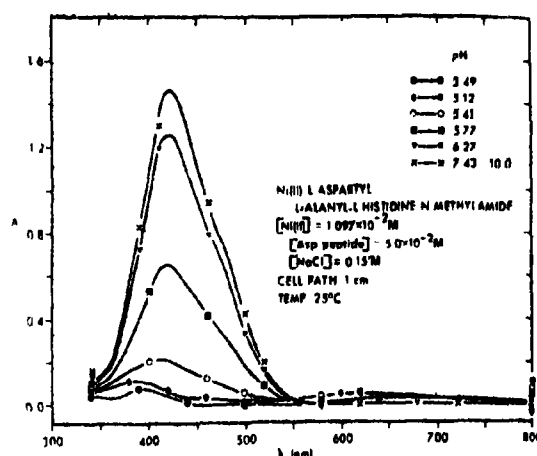
Fig. 6 Visible absorption spectra as a function of pH for the Ni(II)-L-aspartyl-L-alanyl-L-histidyl-N-methyl amide system. [Ni(II)] = 10.97 mM ; [Peptide] = 50 mM in 0.15M NaCl at 25°[24].

These results strongly suggest that the Ni(II)-binding site is located in the NH_2-terminal tripeptide segment of HSA. Further studies with Ni(II)-binding to DSA and its NH_2-terminal model peptide glycylglycyl-L-tyrosine-N-methyl amide showed a lack of binding specificity[28]. There is a histidine residue in the third position of HSA as has been discussed before and it has a greater specificity for Ni(II)-binding. Hence, it appears that the imidazole group is involved in the Ni(II)-binding

To further characterize this site, detailed ^{1}H- and ^{13}C-nmr experiments were undertaken with Ni(II)-binding to AAHNMA[26]. The individual chemical shifts ($\Delta=\delta_{1/1\ complex}-\delta_{free\ peptide}$) for carbons and protons are shown in Fig. 7. The Asp COO^- carbon is affected most of all by Ni(II) binding (Δ=8.32 ppm at pH=9.1) which is consistent with carboxylate-Ni(II) coordination. The imidazole ring system also shows large variations [C(5), Δ=−2.45 ppm]. Upon complexation, the Ni(II)-binding to the NH_2-terminal and COO^- group affects the α carbon (4.69 ppm) more strongly while in the case of β carbon, we observed a shielding effect (−1.73 ppm) at pH 9.1 In the proton nmr spectra, many upfield chemical shifts are observed for imidazole residue. Most significantly, in DMSO-d_6 solution containing Ni(II)-AAHNMA, there is a complete disappearance of Ala and His N-H protons, which confirms the coordination of these two peptide nitrogens. The above results suggest that Ni(II) forms complex with this peptide involving the α-NH_2, N(3) imidazole, two deprotonated peptide nitrogens, and the COO^- group in a pentacoordinated structure as shown by the arrows in Fig. 7. Subsequent studies of Ni(II)-binding to the NH_2-terminal 24-residue peptide fragment of HSA by ^{13}C-nmr technique confirmed the above structure[30].
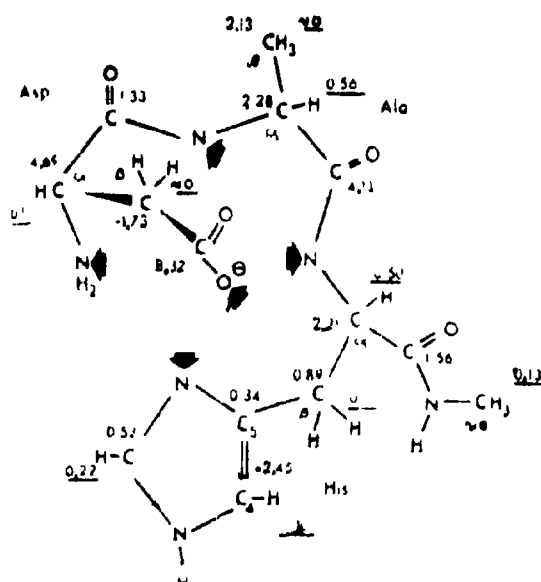
Fig. 7. Chemical shift ($\Delta=\delta_{1/1\ complex}-\delta_{free\ peptide}$) for the 1/1 Ni(II)-L-aspartyl-L-alanyl-L-histidine-N-methyl amide complex in D_2O at *p*H 9.1. Underlined numbers represent ^1H values and numbers without underline show ^{13}C values in ppm. Arrows are directed toward the proposed site of Ni(II)-binding to the peptide[24]

Zinc(II)-binding site of carboxypeptidase .

Carboxypeptidase is a Zn(II)-metalloenzyme which catalyzes the hydrolysis of the carboxyl terminal of peptides and esters. Upon removal of Zn(II), a catalytically inactive apoenzyme results. The role of Zn(II) and other transition metals in the enzymatic activity of carboxypeptidase has been the subject of many investigations[27,28]. The Zn(II)-binding ligands involved in the binding have been identified as His (69), Glu(72) and His(196)[29,30].

Initially, we designed a linear hexapeptide, Gly-L-His-L-Ser-L-Arg-L-Glu-Gly, containing the native sequence 69-72 of carboxypeptidase with glycine on two termini[31]. But the peptide did not show any specificity for Zn(II)-binding. It was thought that a suitable model should include all the three native Zn(II) ligands. A critical survey of several metallo-enzymes, whose crystal structures have been elucidated, revealed the natural occurrence of one to three amino acid residues in between two ligands for the metal-binding. Other ligands originate from a distant part of the molecule. With this consideration, a linear octapeptide containing the three native Zn(II)-ligands with the sequence, Gly-L-Glu-Gly-Gly-L-His-Gly-L-His-Gly, was designed and synthesized[32]. But this peptide also did not show significant specificity for Zn(II)-binding.

At this stage, it was thought that a linear peptide has considerable conformational flexibility. The ligands in the native enzyme are somewhat fixed because of the folding of the protein. Thus, it was thought that the cyclization of the linear peptide may be a means by which binding residues can be brought close to each other. In this manner, certain rigidity can also be introduced in the molecule. Model building by both CPK and Kendrew models showed that the cyclic octapeptide of the same sequence, cyclo(Gly-L-Glu-Gly-Gly-L-His-Gly-L-His-Gly) provide the satisfactory requirements for the Zn(II)-binding geometry. This model retains the native Zn(II)-ligands interspaced by glycine residues. The two imidazole residues and the γ-carboxyl moiety of the glutamyl residue in the model seemed to interact well with the tetrahedral Zn(II).

The cyclic octapeptide was synthesized by high dilution technique from the corresponding linear octapeptide, N-Boc-Gly-γ OBu^t-L-Glu-Gly-Gly-L-His-Gly-L-His-Gly-OBzlNO_2 via the azide method[33]. The linear octapeptide was obtained by coupling of the two tetrapeptide fragments : N-Boc-Gly-γ-OBu^t-L-Glu-Gly-Gly-ONp and L-His-Gly-L-His-Gly-OBzlNO_2. The cyclic peptide was purified to homogeneity The product obtained was ninhydrin negative and Pauli's reagent positive. Further confirmation of this material was obtained by the proton magnetic resonance spectrum in which the various kinds of protons of this peptide were accounted for.

A detailed ^{13}C- and ^1H-nmr investigation was undertaken to determine the Zn(II)-binding ligands of the cyclic octapeptide. The details of the ^{13}C- and ^1H-nmr spectra are shown in Figs. 8 and 9
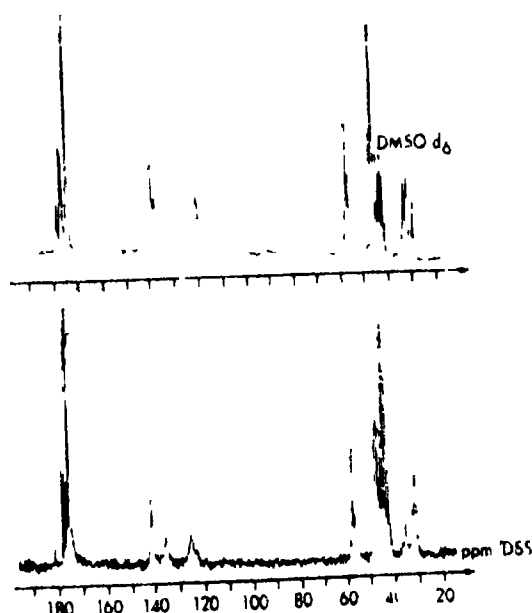
Fig. 8. ^{13}C-NMR spectra (25.16 MHz) of cyclo (Gly-L-Glu-Gly-Gly-L-His-Gly-L-His-Gly) in DMSO-d_6. The upper spectrum is of the free peptide, the lower of octapeptide in presence of Zn(II) (1 : 1)[33]

The effect of increasing concentrations of Zn(II) on the octapeptide in DMSO-d_6 in the range Zn(II)/peptide=1 : 4 to 2 : 1 shows that the Zn(II)-complex is in fast exchange on the nmr time scale. The important observation was the increasing or decreasing shifts with increasing Zn(II) from ratio 1:4 to 1:1 ; beyond this ratio, the shift is unaffected.

Under these circumstances, the results suggest a 1 : 1 complex (Fig. 10).
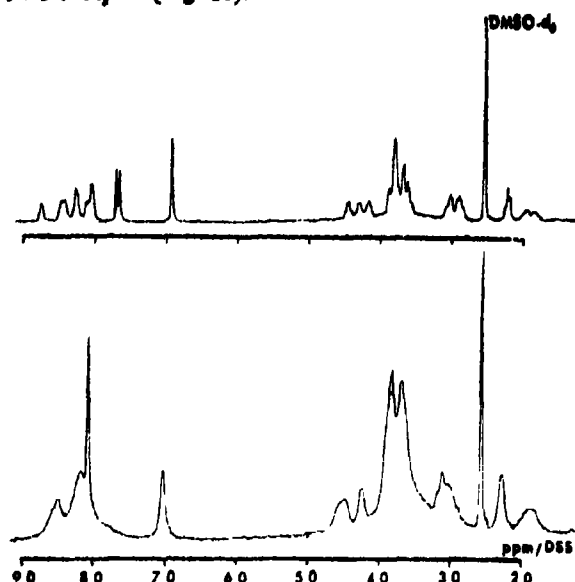
Fig. 9. ^{1}H-NMR spectra (220 MHz) of cyclo (Gly-L-Glu-Gly-Gly-L-His-Gly-L-His-Gly) in DMSO-d_6. The upper spectrum is of the free peptide, the lower of octapeptide in presence of Zn(II) (1 : 1). The scale is downfield from TMS[44].
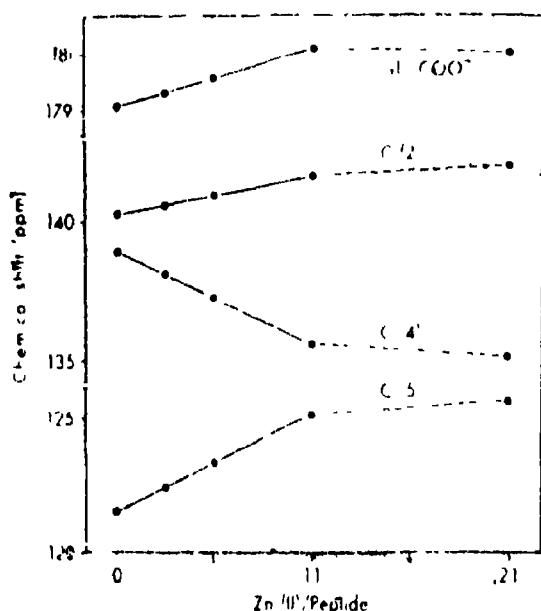
Fig. 10 The variation of the ^{13}C chemical shift as a function of the relative concentration of Zn(II) present. The data were obtained in DMSO-d_6[44].

In Table 5, the chemical shifts of ^{1}H and ^{13}C resonances in cyclo-octapeptide are compared with the corresponding resonances observed in the 1 : 1 complex. In the case of protons, the largest chemical shift changes are observed for the proton resonances of the histidine residues and more particularly C(2)H protons, All the NH resonances are unaffected. Thus, the peptide -NH- group does not participate in coordination. The chemical shi induced on glutamic acid residue are about 0.1 p or less. In the case of ^{13}C resonances, the m dramatic changes in chemical shift occur in t histidine residues and especially in the imidaz ring. The three carbon of the imidazole ring, C(C(4) and C(5), show a large change in chemi shift upon binding to Zn(II). The two methyle of the glutamic residue show a large change chemical shift upon ligating to the metal ion. Bo carbons are shifted downfield (Glu C_γ=0.88 pp

TABLE 5—^{13}C- AND ^{1}H-NMR SHIFTS FOR CYCLO-OCTAPE PTIDE AND 1 : 1 ZN(II)-CYCLO-OCTAPFPTIDE IN DMSO-d_6

	^{13}C		^{1}H	
	cP8[a]	cP8-Zn(II)	cP8	cP8-Z(II)
Glu CH_2 β	31.38	32.07	1.89	1.87
His CH_2 β	33.72	32 07	2 89	2 97
	34 03		3.02	3.15
Glu CH_2 γ	35 23	36 11	2.22	2.32
Gly CH_2	47.88	47 89	3.86	3.86
			3.82	3.82
			3.67	3.67
			3.62	
Glu CH α	57 81	56.81	4.16	4 21
His CH α	58.80	57.89	4.30	4 43
			4 46	4 66
C(5)-H	121 36	125 02[b]	6 92	7 02
	121.80			
C(4)-H	138 98	135 49[b]	—	–
C(2)-H	140 11	141 31	7.65	8.08
			7.70	
Gly CO	174.55	174 43	—	—
	175.00	174.70		
		174.90		
His CO	176 80	175.76	—	—
	177.41	176 64	—	—
Glu CO	177.66	177 53		
Glu COO⁻	179 08	181 09	—	—

a cP8 : cyclo-ocatpeptide.

b Linewidth at half-height 60 Hz [C(4)-H] and 36 Hz [C(5)-H]

Glu C_β=0 69 ppm). The carboxyl resonances fro glycine are essentially unaffected upon Zn(I binding. But the carbonyl atoms of glutamic ar the two histidine residues shift upfield −0.13, −1.(and −0.77 ppm, respectively, upon complexatio The most significant observation is the deshieldi effect (Δ=2.01 ppm). From these observation it is clear that the largest chemical shifts occur f the two imidazole rings and for the glutam
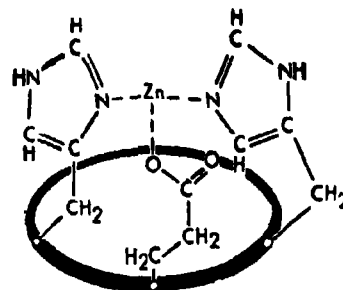
Fig. 11. Structure of the Zn(II)-binding to the designe cyclo-octapeptide as deduced from the nn studies[44].

carboxyl group. The results demonstrate that both the imidazoles of the two histidine residues and the carboxyl side chain of the glutamic acid residue of the cyclo-octapeptide are coordinated to Zn(II) as shown in Fig. 11.

Zinc(II)-binding site of carbonic anhydrase:

Carbonic anhydrase is a Zn(II) containing metalloenzyme and the catalytic activity of the enzyme is linked to the presence of Zn(II) ion[84]. The biologically relevant activity of the enzyme is the reversible hydration of carbon dioxide although it is known to catalyze a variety of hydration reactions, such as the hydration of various aldehydes, and carboxylic, sulfonic and carbonic esters. Zinc(II) in the enzyme is bound to the histidine residues, which in human B isozyme are: His-94, His-96, and His-119[85]. The coordination geometry about the Zn(II) is distorted tetrahedral with the fourth position occupied by a water molecule.

Considering the known structure of the Zn(II)-binding site of carbonic anhydrase, the simplest possible peptide model which may be proposed for this metal binding site is one which contains three histidyl residues linked in a manner that would enable formation of the base of a tetrahedron when Zn(II) complexation occurs. Similar considerations as those followed in the design of carboxypeptidase Zn(II)-binding model resulted in the designing of a cyclic heptapeptide molecule: cyclo(Gly-L-His-Gly-L-His-Gly-L-His-Gly)[86]. Model building by both CPK and Kendrew models indicated that the three histidines of the above cyclic heptapeptide have the ability to interact with the Zn(II) to form a tetrahedral complex.

The cyclic heptapeptide was synthesized from the linear heptapeptide, Gly-L-His-Gly-L-His-Gly-L-His-Gly-OH, which in turn was obtained by coupling of the fragments, viz., BOC-Gly-L-His-Gly-N_3 and L-His-Gly-L-His-Gly-OBzlNO_2 followed by deblocking of amino and carboxyl protecting groups. Conversion of the linear heptapeptide to the azide by treatment with diphenylphosphoryl azide was followed by cyclization in high dilution. The homogenous material was found to be ninhydrin negative The nmr spectrum of the material upon integration indicated the proper ratios of various kinds of protons to be expected of the cyclic heptapeptide[86].

The metal titration studies show that the magnitude of the chemical shift perturbations induced by Zn(II) increases in increasing metal ion concentration from Zn(II)/peptide ratio 1 : 4 to 1 : 1 ; beyond this ratio, the shift is unaffected. Thus, the cyclic heptapeptide forms a 1 : 1 complex with Zn(II). Similar studies were undertaken by ^{13}C-nmr technique. Fig. 12 shows the relationship between the ratio of Zn(II)-peptide to the change in chemical shift of the C(2), C(4) and C(5) imidazole carbons of the cyclic peptide. The change in chemical shift for all the carbons is linear to a ratio of 1 : 1, following which it seems to level off. This result is consistent with a 1 : 1 complex of Zn(II)-cyclopeptide.
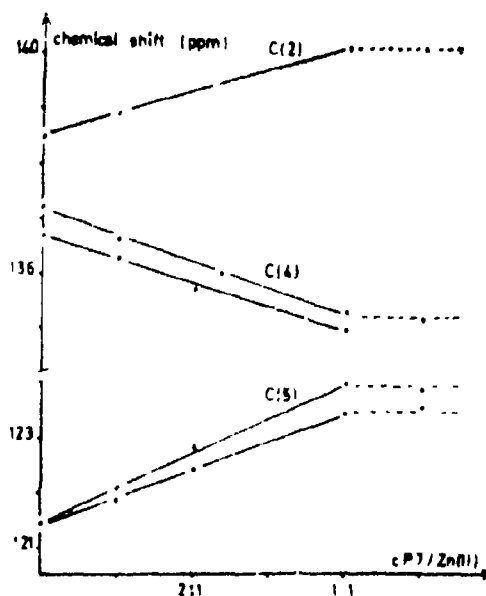
Fig 12. The variations of the ^{13}C chemical shift in DMSO-d_6 as a function of the cyclic heptapeptide/Zn ratio[86]

The ^{1}H- and ^{13}C-nmr spectra of free cyclic heptapeptide and Zn(II)-bound peptide are shown in Figs 13 and 14 The chemical shifts of ^{1}H and ^{13}C resonances in cyclopeptide are compared with the
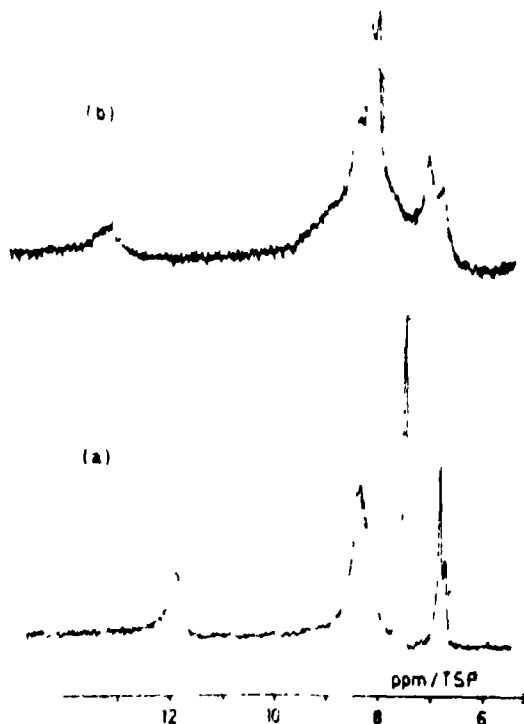
Fig. 13. A portion of the ^{1}H-nmr spectrum obtained in DMSO-d_6 at 250 MHz showing the resonances of the exchangeable N-H protons and imidazole protons of cyclic heptapeptide (a) and its 1 : 1 complex with Zn(II) (b)[86].
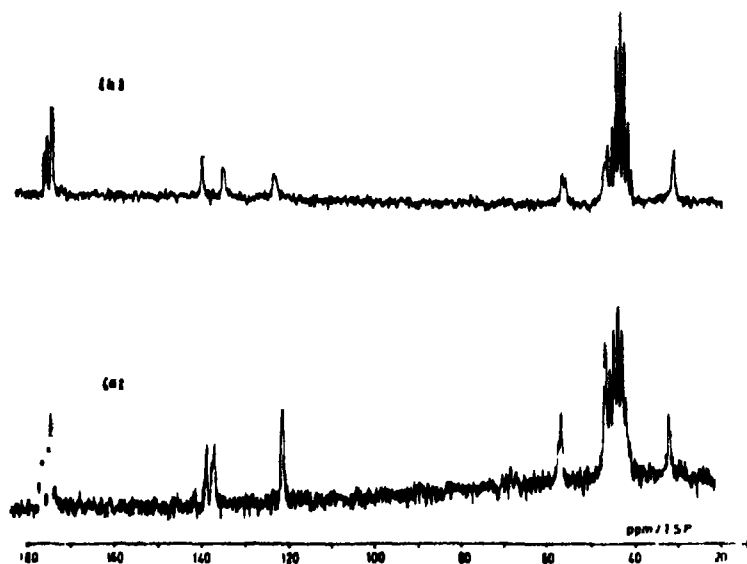
Fig. 14. ^{13}C-NMR spectra (22.63 MHz) of cyclo(Gly-L-His-Gly-L-His-Gly-L-His-Gly) in DMSO-d_6, in the (a) absence and (b) presence of 1·1 Zn(II)[a]

corresponding resonances observed in the 1 : 1 complex in Table 6. The changes in the chemical shift of the proton of imidazole are relatively large, indicating that this ring is involved in the complexation. The largest downfield shift occurs for the imidazole N(1)-H proton (Δ=1.34 ppm). The peptide -NH- resonances are clearly observable and almost unaffected. Consequently, none of these nitrogens can serve as a ligand.

TABLE 6—^{13}C- AND ^{1}H-NMR CHEMICAL SHIFTS FOR CYCLO-HEPTAPEPTIDE AND 1 : 1 ZN(II)-CYCLO-HEPTAPEPTIDE IN DMSO-d_6

	^{13}C		^{1}H	
	cP7[a]	Zn(II)-cP7	cP7	Zn(II)-cP7
His CH_2 β	32 25	31 40	2.93	3 11
			2 97	
Gly CH_2	46.81	46.87	3 47	3 55
	47.00	47 04	3 60	
			3.74	
His CH α	57.21	56.30	4.36	4.52
	57.67	57.02	4 48	
C(5)-H	121 45	123.41	6.79	6.90
		123.99	6.88	7 16
C(4)-H	136 67	135.04	—	—
	137.25	135.40		
C(2)-H	138 49	140 20	7.54	8.16
			7 59	8.28
N(1)-H	—	—	11.88	13.22
Gly CO	173 63	173.80	—	—
	173 93	173.90		
		174.06		
His CO	175.42	175.10		
	176.13	175.42		
		175 87		

[a] cP7, cyclo-heptapeptide.

By addition of one equivalent of Zn(II) to the peptide, the imidazole residue is the most affected as shown by the ^{13}C-nmr spectra. The C(2), C(4) and C(5) carbon resonances of this group are dramatically affected and show a very large change in chemical shift after complexation. In fact, all three imidazole residues are affected in the same way and suggest that these residues of cyclo-heptapeptide are ligands. Both C(2) and C(5) carbons move downfield (Δ=1.71 and 1.96, 2.54 ppm, respectively) while C(4) moves upfield upon complexation (Δ=−1.63 and −1.85 ppm). Shifts of similar magnitude and sign have been observed for the imidazole residue of histidine when this amino acid residue in a peptide binds to Zn(II)[85,87]. There are changes in His C_α and His C_β, which are all neighbours of the imidazole ring. The Gly C_α carbon signals and the Gly carbonyl resonances appear to be unaffected by metal complexation whereas the carbonyl carbon atoms of the three histidine residues move ~0.50 ppm upfield on complexation. From these results, we can conclude that the designed cyclic heptapeptide binds a single Zn(II) ion in 1 : 1 complex and that the binding site for Zn(II) is the N(3) nitrogen of the three imidazole residues as shown in Fig. 15.
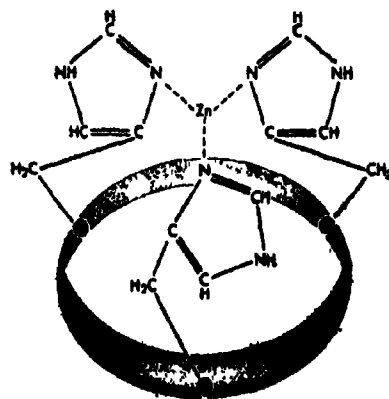
Fig. 15. Structure of the Zn(II)-binding to the designed cyclic heptapeptide as deduced from the nmr studies.

Conclusion :

The results discussed above confirm the concept of molecular design to mimic the metal-binding sites of biological macromolecules[39]. However, several interesting facts have emerged from these studies. In the investigations of the Cu(II)-transport site of HSA, we initially designed two peptides, GGH and GGHNMA. Both the peptides demonstrated a remarkable similarity with the Cu(II)-transport site of HSA. But it was not until the native sequence peptide AAHNMA was synthesized and the Cu(II)-binding studies were carried out did we recognize the full implication of the carboxyl side chain of the NH_2-terminal aspartyl residue of HSA. Extensive chemical and physical studies with the native HSA molecule failed to detect the involvement of the carboxyl group in the coordination of Cu(II). The same holds true with the Ni(II)-transport site of HSA. Although these experiments helped in the structural elucidation of the Cu(II)-transport site of HSA, the functional aspects of this site are still unclear. It is possible that some residues which may not be directly bonded to the metal, yet close enough, could influence the dynamics of the Cu(II)-transport. In designing models for the Zn(II) binding sites of carboxypeptidase and carbonic anhydrase, it is clear that the cyclic peptides afforded both the rigidity and the ligand binding geometry of the native metal binding sites. In these models, too, the functional aspects of the metal binding sites are not considered and hence no catalytic activity of the enzyme can be expected in these molecules. One should also bear in mind that in none of these models does the native microenvironment around the metal binding site appear. Thus, one must use caution to interpret the model studies in relation to defining the native metal binding sites. However, peptide molecules belong to an important class of models to probe the metal binding sites and a careful analysis of the results should provide critical information about the structure of the metal-binding sites of proteins and enzymes.

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Separation of Th(IV) in Aqueous Glycine Medium by Cation Exchange Chromatography

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Through cation exchange column chromatography using Dowex 50W-X8 (Na^+ form, 100-200 mesh) in aqueous 0 20 *M* glycine media, analytical conditions predicted from the distribution coefficient (*K*), have enabled the separation of a wide concentration of Th(IV) from U(VI), Al(III) Cr(III), Fe(III), La(III), Ce(III), Ca(II), Sr(II), Ba(II), Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), Ag(I), Cu(II) or Hg(II). The following ternary mixtures were also resolved: Th(IV)-Cu(II)/Hg(II)-U(VI)/Al(III)/Cr(III)/Fe(III)/La(III)/Ce(III)/Ca(II)/Sr(II)/Ba(II)/Mn(II)/Co(II)/Ni(II)/Zn(II)/Cd(II)/Pb(II)/Ag(I) In all the separations column kinetics was found to be favourable, though the separation of Th(IV) was almost but not quite quantitative. Values of *K*, elution characteristics of metal ions, elution curves and results of the resolution of a number of mixtures are presented

MOST of the reported methods[7] for the separation of thorium by ion exchange in HCl, HNO_3 or H_2SO_4 media suffer from disadvantages rendering the resolution of mixtures containing a number of metal ions difficult The slow kinetics of ion exchange in the mineral acids is perhaps a serious drawback, which results in tailing in the chromatograms. For example, anion exchange chromatography in 5-6 *M* HNO_3 is highly selective for Th(IV)[1,2] but tailing of U(VI) and a few other metal ions limits the application of this method. Considerably better kinetics, though not excellent, was obtained in 0.60 *M* HNO_3 containing 55% acetone[7,8]. Also, in the case of cation exchange separations of Th(IV), eluting agents such as 3 *M* H_2SO_4[9,12] or 0.50 *M* oxalic acid[11] are inefficient because kinetics is slow and for the quantitative recovery of Th(IV), the resin must be ignited to ash[14,15,16] and Th(IV) determined in the residue. However, Strelow *et al*[17] were able to devise a method for the separation of Th(IV), which does not require ashing.

Glycine is a versatile complexant[18] and among the separations described using glycine, are those of Zn(II)-Cd(II)[22] and of Cu(II)-Co(II)[4]. A chelating exchanger was used by Hering[5] for studying the ion exchange behaviours of Fe(III) Cu(II), Ni(II), Co(II), Mg(II) and K(I). Glycine and other amino acids along with other complexants were used as retaining agents for the separation of several less familiar elements on NH_4^+-form nuclear sulphonic acid exchanger at 85-90°[21]. Jercan and Dinoiu[6] reported the concentration and separation of U(VI) from diverse ions using Dowex 2X-8 and Vionite AT-1 anion exchanger in glycine (*p*H>3.4 to <6) solution containing α,α'-bipyridyl.

In this work, a systematic study has been done on the possibility of concentration and separation of Th(IV) in aqueous glycine medium. The following metal ions, U(VI), Al(III), Cr(III), Fe(III), La(III), Ce(III), Ca(II), Sr(II), Ba(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II) and Ag(I) were also studied for obtaining the analytical conditions under which Th(IV) may be separated from mixtures The resin used was strongly acidic Dowex 50W-X8. On the basis of the *K* values, specific separation of Th(IV) from 18 other metal ions was achieved by column chromatography. A wide range of concentrations of glycine and Th(IV) were studied for the separation but only one typical set is included here. Better recovery of Th(IV) occurs when glycine is below 0.4 *M*, while the recovery shows a fall if the concentration of glycine is higher. *K* values, elution behaviour of metal ions, elution curves and results of the resolution of various mixtures are reported in this communication.

Experimental

Material:

(a) *Water*: De-ionised distilled water was used in all the experiments.

(b) *Metal ion solution*: Aqueous 0.06-0.20*M* solutions of U(VI), Al(III), Cr(III), La(III), Ca(II), Sr(II), Ba(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Ag(I) were prepared from reagent grade nitrate samples (BDH AnalaR or Johnson Mathey) Solutions of Hg(II), 0.10 *M* in 0.10 *M* glycine, and of Th(IV), 0.05 *M* in 0.05 *M* glycine were prepared from their nitrate samples (BDH AnalaR) directly in glycine solution. Fe(III) solution, 0.06 *M* in 0.06 *M* glycine was prepared from ammonium iron(III) sulphate directly in aqueous glycine solution. Cerous chloride (Johnson Mathey) was used to prepare aqueous solution of Ce(III). The solutions were standardised by determining the metal contents[8,19,20].

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(c) *Glycine solution* : 2.0 *M* stock solution of glycine (E. Merck, G.R.) was prepared in water. Freshly prepared solutions were used.

(d) *Ion exchange resin* : Strongly acidic polystyrene based sulphonic acid Dowex 59W-X8 (Na^+-form, 100-200 mesh) was washed in a column with *ca* 0.2 *M* EDTA solution (*p*H 8-10) and then with water. The resin in the Na^+-form was obtained by passing a large excess of *ca* 10% NaCl solution through the column and then washing with water until free from chloride ions. The resin in the Na^+-form was air dried on a sintered bed by applying suction and was stored in an air tight bottle. The capacity and water content were found to be 3.04 meq/g and about 21%, respectively

Apparatus :

(a) *Equilibration studies* : A wrist motion micriod flask shaker (Griffin & George), operating on 220 V/50 cycles A.C. mains was used for shaking the solutions with the resin in 100 ml pyrex flasks

(b) *p*H *measurements* : A Leeds and Northrup *p*H meter was used for *p*H measurements.

Distribution studies :

An appropriate amount of metal ion (about 30% of the total exchange capacity of resin) solution and aqueous glycine of the desired concentration (0 04 to 1.60*M*) were mixed and 1 g of resin was added. This was shaken for 1 hr and the resin was filtered off. The metal content was determined in the solution phase. Glycine did not interfere in the estimation of metal ions. *K* was determined using the relationship, *K*=meq metal per g of resin/meq metal per ml of solution.

All experiments were performed at least in duplicate, at 30±2°, and the average values are recorded (Table 1). The relative experimental error in the determination of *K* values was usually ±5 to 10%.

Results and Discussion

In general, *K* values of most of the metal ions studied decrease with an increase in glycine concentration from 0 04 to 1.60 *M* (Table 1). Complexation with glycinate ion is, perhaps, the dominant factor which governs the trend and magnitude of the sorption. The cation exchange sorption of a metal ion decreases as the charge on the species formed changes from a small positive value to zero and finally becomes negative. Previous studies[8] has confirmed that an effective decrease in the sorption is not necessarily accompanied by the formation of a negatively charged species.

Water molecules coordinated with metal ions are generally replaced by glycine as its concentration is increased, resulting in the formation of small positive charged or neutral species in most of the cases, leading to the decrease of *K* values. Further increase of glycine concentration perhaps favours the formation of neutral species as indicated by appreciably high values of *K*. The high values of *K* even at higher concentrations of glycine, in almost all metal ions except Th(IV), Cu(II) and Hg(II), suggest that metal ions or complex ions with a low charge have higher affinity for cation exchanger than glycine in aqueous medium.

Though Th (IV) has the highest positive charge amongst the metal ions, it shows the lowest affinity

TABLE 1—DISTRIBUTION COEFFICIENTS IN AQUEOUS GLYCINE

Distribution coefficients (*k*)

Metal Ion	Conc. of aqueous glycine (*M*)						
	0.04	0.12	0 20	0.40	0 64	1.00	1.60
Al(III)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Ca(II)	1290	1080	1060	1220	1290	1080	1220
Cr(III)	1620	1240	1800	2460	—	890	800
Mn(II)	2270	2530	2270	1970	1740	1890	1890
Fe(III)	2580	2010	1850	1150	670	560	480
Co(II)	3260	1820	2080	1200	680	420	270
Ni(II)	2600	1050	690	320	190	110	60
Cu(II)	340	90	49	28	8.8	4.9	2.2
Zn(II)	1040	950	760	560	400	310	240
Sr(II)	1720	1600	–	1410	—	—	4050
Ag(I)	280	280	280	260	240	200	170
Cd(II)	1250	1050	1050	1050	1050	780	780
Ba(II)	1120	1040	–	1690	—	—	2370
La(III)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hg(II)	1690	230	80	25	12	6.0	3.4
Pb(II)	1440	1360	1360	1760	2750	8310	12400
Ce(III)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Th(IV)	3.2	3.0	3.2	2.9	4.2	5.2	6.3
U(VI)	(a)	(a)	(a)	(a)	(a)	(a)	630

a = Very high value.

for cation exchanger as the amount of glycine is increased. In the case of Cu(II) and Hg(II) the *K* values decrease appreciably with the increase in glycine concentration and at 1.60 *M* glycine the *K* values are even lower than that for Th(IV). This behaviour shown by Cu(II) and Hg(II) metal ions is due to their pronounced complexing tendency with glycine, resulting in the formation of perhaps negatively charged species[10].

Prediction of separation possibilities :

K values suggest the utility of glycine for the separation of Th(IV) from other metal cations. Th(IV) should follow the feed effluent because of low affinity for the exchanger and other metal ions should be retained onto the resin bed due to higher affinity. The separation of Th(IV) from Cu(II) or Hg(II) is noteworthy, since these cannot be achieved at higher glycine concentrations (>0.64 *M*) because of almost identical *K* values. Below 0.64 *M* glycine, Th(IV) should follow the feed effluent and the strongly retained Cu(II) or Hg(II) may thereafter be removed with higher amounts of glycine.

Separation of binary and ternary mixture :

Column chromatographic separations of Th(IV) from other metal ions were achieved under the conditions predicted from batch experimentation. The following procedure was adopted :

Preparation and pretreatment of resin bed : The resin slurry (~5 g) was prepared in water from prepurified and washed Na^+-resin. It was transferred to the graduated column (~65 cm long with internal diameter ~0.85 cm). The height of the resin bed was about 8.0 cm. It was then treated with 0.10 *M* or 0.20 *M* glycine solution, as the case is.

Preparation of feed and sorption : The feed, 25 ml in 0.20 *M* glycine, was prepared in duplicate by mixing known amounts of Th(IV) and one of the other cations studied. The feed was passed through the column at the controlled flow rate of 1.0 ± 0.5 ml/min. Feed effluent was collected from the beginning of the sorption.

Elution : The sorption was followed by the quantitative elution of the components of the binary mixtures. The very weakly held Th(IV) was eluted with 40 ml of 0.20 *M* glycine (including 25 ml of feed effluent). The break-through of strongly sorbed other metal ions [except Cu(II) and Hg(II)] were not observed even after the passage of 125 ml of 1.0 *M* glycine (Table 2). Cu(II) or Hg(II) was recovered with 105 and 95 ml of 1.6 *M* glycine while other ions were stripped off with the help of other eluents. Al(III), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II) and Ce(III) were eluted with about 80 ml of 2.5 *M* HCl, Ag(I) with 65 ml of 2.5 *M*

TABLE 2—ELUTION CHARACTERISTICS OF METAL IONS ON DOWEX 50W-X8 COLUMN

Metal	BTV(ml)	VEP (ml)	TEV (ml)	Eluting agent
Th(IV)	5	~20	40	0.20*M* Glycine
Cu(II)	15	45	105	1.6*M* Glycine
Hg(II)	5	30	95	—do—
Al(III)	>125	–	–	2.5*M* HCl
Cr(III)	>125	–	–	—do—
Fe(III)	>125	–	–	—do—
La(III)	>125	–	–	—do—
Ce(III)	>125	–	–	—do—
Co(II)	>125	–	–	—do—
Ni(II)	>125	–	–	—do—
Zn(II)	>125	–	–	—do—
Cd(II)	>125	–	–	—do—
Mn(II)	>125	–	–	—do—
Ca(II)	>125	–	–	3*M* NH_4OAc
Sr(II)	>125	–	–	2*M* NH_4OAc
Ba(II)	>125	–	–	4*M* NH_4OAc
U(VI)	>125	–	–	1*M* NH_4OAc
Pb(II)	>125	–	–	4*M* NH_4OAc
Ag(I)	>125	–	–	2.5*M* HNO_3

BTV - Breakthrough volume. VEP - Volume elution peak TEV - Total elution volume.

TABLE 3—RESULTS OF THE SEPARATION OF Th(IV) FROM A NUMBER OF METAL IONS

Th(IV) taken - 59.17 mg

Taken: Other Metal Ions*	Taken: mg	Number of Determinations	Recovery of Th (IV) in (%)
Ag(I)	56.63	6	96.20
Mn(II)	27.42	6	95.90
Co(II)	29.46	6	96.01
Ni(II)	27.80	6	96.10
Cu(II)	31.77	8	96.00
Zn(II)	32.84	6	96.20
Ca(II)	20.10	6	96.30
Cd(II)	56.76	6	96.04
Hg(II)	100.80	8	96.08
Pb(II)	104.63	8	96.16
Sr(II)	25.66	6	96.12
Ba(II)	63.59	6	96.20
La(III)	45.70	6	95.98
Ce(III)	32.07	6	96.04
Al(III)	8.97	6	96.15
Fe(III)	17.51	8	96.20
Cr(III)	17.19	6	96.06
U(VI)	120.17	6	96.06

*The recovery of these were ~100%.

HNO_3, Ca(II) with 75 ml of 3 *M* NH_4OAc and Pb(II) with 75 ml of 4.0 *M* NH_4OAc. The results of the separations are reported in Table 3.

Th(IV) can also be separated from other metal ions [except Cu(II) and Hg(II)] at higher concentration (>1.0 *M*) of glycine. But the recovery of Th(IV) has been found to be only about 80-85%. The recovery may be enhanced upto 96% if the separation is done at lower (<0.20 *M*) concentration of glycine and hence all separations were achieved in 0.20 *M* glycine. In all the separations column kinetics is highly favourable, the recovery is good but not quite quantitative perhaps due to very slow ligand exchange rates.

Elution curves: Figs. 1 and 2 represent the elution curves for the resolution of the following mixtures: Th(IV)-Fe(III)/Ce(III)/Pb(II) and Th(IV)-Cu(II)/Hg(II), respectively. The concentration is represented in terms of ml of 0.01 *M* EDTA. Volume of the effluent in the figures also include the volume passing out of the resin bed from the feed
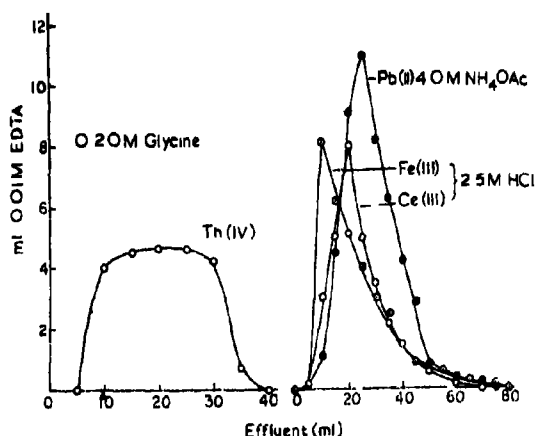
Fig. 1. Elution curves: Th(IV)-Fe(III)/Ce(III)/Pb(II)
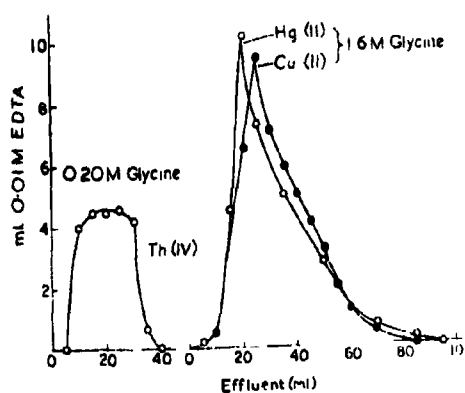
Fig. 2. Elution curves: Th(IV)-Hg(II)/Cu(II).

The separation between Th(IV) and Cu(II) or Hg(II) along with other cations at lower glycine concentration (0.04-0.20 *M*) and of these three from other cations at higher glycine concentration (1.0-1.6 *M*) indicated the possibility of a number of ternary separations: Al(III)/Ca(II)/Cr(III)/Mn(II)/Fe(III)/Co(II)/Ni(II)/Zn(II)/Sr(II)/Ag(I)/Cd(II)/Ba(II)/Pb(II)/U(VI)/La(III)/Ce(III)-Cu(II)/Hg(II)-Th(IV).

For chromatographic separations of ternary mixtures, the feed was prepared in 0.1 *M* glycine by mixing any three of the above mentioned cations. Th(IV) followed the feed effluent whereas other metal ions were held onto the resin bed with considerable variation in sorption. Recovery of Th(IV) was achieved with 0.10 *M* glycine. Th(IV) exhibits almost similar behaviour as in 0.20 *M* glycine because it has almost identical *K* values in 0.04 to 0.20 *M* glycine. After the complete elution of Th(IV), not too strongly held Cu(II) or Hg(II) was eluted with 1.60 *M* glycine and finally the most strongly retained metal ions were desorbed with HCl, HNO_3 or HN_4OAc, as the case may be.

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Effect of Substituents on the Relative Stabilities of Fe(III) Complexes of Substituted Salicylic Acids

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The stability constants of Fe(III) complexes of salicylic acid (SA) and ten of its substituted derivatives were determined at constant ionic strength using spectrophotometric measurements. Fe(III)-SA system was taken as a reference for comparing the difference in the acid dissociation constants (ΔpK) and stability constant values ($\Delta \log K$). A parallelism is observed, though the magnitude of $\Delta \log K$ is less than ΔpK. While the substitution of an electron donor group increases the stability constant, it decreases the value of the apparent equilibrium constant. Similarly, the electron withdrawing groups have opposite effect on these two parameters. A hypsochromic shift in the absorption maximum (λ_{max}) of 1 : 1 complex is observed when an electron withdrawing group is substituted in the nucleus of the reference ligand, whereas other groups (or an atom like Hg) give a bathochromic shift. However, exact correlation between $\Delta \lambda_{max}$ and $\Delta \log K$ or ΔpK was not observed.

IRON(III), due to its pronounced affinity for ligands containing oxygen, forms several coloured complexes with salicylic acids[1-15]. Thus, salicylic acid and sulphosalicylic acid have extensively been used as colorimetric reagent[16-18] for iron(III). Similar to Fe(III)-phenol complexes[19-20], the colour of Fe(III)-salicylates depends on the various substituent groups attached to salicylates. The substitution effect influences the dissociation constants[21] and consequently the metal ligand stability constants. Hence, it was thought of interest to study the influence of substitution on the stability constants and on the absorption spectra of Fe(III)-salicylates. For this purpose, salicylic acid and ten of its substituted derivatives were chosen as ligands.

Experimental

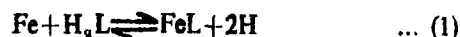
Methods :

Reagent grade samples of the following salicylic acids were employed : (i) 2-Hydroxy benzoic acid (SA), (B.D.H.), (ii) 2-Hydroxy 3-methyl benzoic acid (oCA), (B.D.H.), (iii) 2-Hydroxy 4-methyl benzoic acid (mCA), (K and K Lab), (iv) 2-Hydroxy 5-methyl benzoic acid (pCA), (K and K Lab), (v) 2-Hydroxy 5-nitro benzoic acid (NSA), (Fluka), (vi) 2-Hydroxy 5-chloro benzoic acid (CSA), (Fluka), (vii) 2-Hydroxy 5-sulpho benzoic acid (SSA), (E. Merck), (viii) 2-Hydroxy 3-methyl 5-sulpho benzoic acid (SoCA), (ix) 2-Hydroxy 4-methyl 5-sulpho benzoic acid (SmCA), (x) 2-Hydroxy 3-sulpho 5-methyl benzoic acid (SpCA) and (xi) 2-Hydroxy 3-mercury 5-sulpho benzoic acid (HgSSA). The acids (viii) to (xi) were prepared as described earlier[22].

All the acids were purified by several recrystallizations before use. Aqueous solutions were prepared by direct weighing, using CO_2-free water. A stock solution of ferric chloride in dilute $HClO_4$ was prepared and standardised titrimetrically against standard dichromate solution. CO_2-free NaOH and $HClO_4$ solutions were used for bringing the pH at the desired value. Solutions of acids and alkalis were standardised by conventional titrimetric methods. $NaClO_4$ was used as a background electrolyte.

Procedure :

In the pH range 1-3.5, the reaction between Fe(III) ion and salicylic acids (H_2L) takes place as follows :

$$Fe + H_2L \rightleftharpoons FeL + 2H \quad \ldots (1)$$

Charges are omitted for simplicity.

At constant pH, the apparent equilibrium constant can be expressed as :

$$K'_1 = \frac{[Fe\,L]}{(Fe^\circ - [Fe\,L])\,(L^\circ - [Fe\,L])} \quad \ldots (2)$$

Fe° and L° being the initial concentration of iron(III) and ligand, respectively.

The stability constant is defined as

$$K_1 = \frac{[Fe\,L]}{[F]\,[L]} = K'_1\,\phi \quad \ldots (3)$$

where

$$\phi = 1 + \frac{[H]}{K_2^H} + \frac{[H]^2}{K_1^H K_2^H} \quad \ldots (4)$$

K_1^H and K_2^H are the dissociation constants (concentration quotient) of ligand for carboxyl and phenolic groups, respectively. Knowing the values of K'_1, K_1^H, K_2^H and [H], K_1 can be calculated from equation (3) at a particular ionic strength.

To find out K'_1 at a definite pH value (2.35 ± 0.05), the molar absorptivity, ϵ, for ML species at

λ_{max} was determined by elimination method[22]. Taking average value of ϵ, K'_1 was calculated at ionic strength of 0.1 from

$$K'_1 = \frac{\epsilon A}{(\epsilon M^o - A)(\epsilon L^o - A)} \quad \ldots (5)$$

where A is absorbance value at λ_{max}.

Using K^H_1 and K^H_2 at I=0.1, determined by the method as described earlier[21], log K_1 was calculated. The relevant data of each system are summarised in Table 1.

0.1, the pH of the solution was varied in the range 1.4-3.2 by adding different amounts of $HClO_4$ and K_1 values were determined. It is observed that there is no appreciable change in K_1 values in the pH range 1.4-2.0, but above pH 2.0, the value decreases, probably due to the hydrolysis of the uncomplexed Fe(III). The effect due to hydrolysis can be accounted for by multiplying the right hand side of equation (3) by the correction factor[24] $(1+K_h/[H])$, where K_h is the first stage hydrolysis constant for Fe(III), the value[25] of K_h being 2.34×10^{-3} at I=0.1. Consistency is then observed in the values of K_1 (the corrected values are shown within the parenthesis in Table 1).

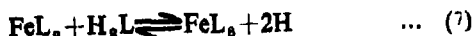
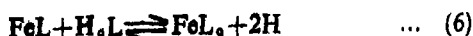
TABLE 1—DISSOCIATION CONSTANTS OF LIGANDS AND STABILITY CONSTANT OF Fe(III)-COMPLEX AT IONIC STRENGTH OF 0.1

Ligand	pK^H_1	pK^H_2	λ_{max}	ϵ_{max}	log K'_1	log K_1	ΔpK	Δ log K'_1	Δ log K_1	$\Delta\lambda_{max}$
SA	2.81	13.24	530	1660	4.70	16.19 (16.37)*	–	–	–	–
oCA	2.84	14.14	556	1660	4.34	16.75 (16.93)	−0.93	+0.36	−0.56	−26
mCA	2.94	13.54	534	1663	4.61	16.49 (16.67)	−0.43	+0.09	−0.30	−04
pCA	2.87	13.74	560	1852	4.62	16.05 (16.83)	−0.56	+0.08	−0.46	−30
NSA	1.90	9.89	496	2097	5.09	12.76 (12.94)	+4.26	−0.39	+3.43	+34
CSA	2.43	12.50	536	1909	4.76	15.25 (15.43)	+1.12	−0.06	+0.94	+06
SSA	2.44	11.90	506	1931	5.00	14.60 (14.78)	+1.71	−0.30	+1.59	+24
SoCA	2.54	12.58	530	2116	4.70	15.34 (15.52)	+0.93	0.0	+0.85	0
SmCA	2.67	12.33	510	2177	4.76	15.23 (15.41)	+1.05	−0.06	+0.96	+20
SpCA	2.52	13.47	546	2213	4.83	16.34 (16.52)	+0.06	−0.13	−0.15	−16
HgSSA	2.43	12.03	514	2038	5.08	15.10 (15.28)	+1.59	−0.38	+1.09	+16

*Values within parentheses include correction factor for hydrolysis of Fe(III)

At higher pH values (above 3.5), higher species of the complex are formed as evident from the study of isosbestic points on absorption spectra at different pH values. The formation of higher species takes place as follows :

$$FeL + H_2L \rightleftharpoons FeL_2 + 2H \quad \ldots (6)$$

$$FeL_2 + H_2L \rightleftharpoons FeL_3 + 2H \quad \ldots (7)$$

At pH 4 and above, considerable hydrolysis of Fe(III) takes place and consequently the stability constant values for higher species were not determined.

All pH measurements were made with a Universal pH meter (Redelkis OP-204, Hungary) with glass and calomel electrodes. The absorption spectra were recorded on Perkin-Elmer 137 UV-Vis or SF-4 USSR spectrophotometers. Measurements were done at room temperature at 25±1°

Results and Discussions

To study the effect of pH on the stability constant of ML species, solutions of Fe(III) ion and the ligand were prepared by mixing them in a 1 : 1 ratio. While the ionic strength was maintained at

For examining the effect of substitution, Fe(III)-SA system was taken as reference for comparison with other systems. The difference in the values of $pK^H_1K^H_2$, log K'_1, log K_1 and λ_{max} were expressed as ΔpK, Δ log K'_1, Δ log K_1 and $\Delta\lambda$, respectively (Table 1). It is noted that the sign (+ or −) of pK and the corresponding Δ log K_1 is identical. However, Δ log K_1 value is smaller in magnitude when compared to ΔpK. A linear plot of log K_1 vs pK^H_1 K^H_2 with a positive slope (< 1) is obtained. However, a small departure is observed in the case of Fe(III)-SpCA systems.

Equation (3) can be written as :

$$\log K_1 = \log K'_1 + \log\phi \quad \ldots (8)$$

ϕ is a function of K^H_1 and K^H_2 and hence at a particular pH the value of log ϕ increases with the increase in pK^H_1 K^H_2 value. The value of log K'_1, however, decreases with the increase in $pK^H_1K^H_2$. Due to this opposing influence, the net increase (or decrease) in log K_1 value is significantly less than that of ΔpK^H_1 K^H_2.

In equilibrium (1), both hydrogen as well as the metal compete for L. If the dissociation constant is large (smaller value of $pK_1^HK_2^H$), [L] available for Fe(III) to form the complex is also more. Consequently at a given pH, log K_1' is higher. log K_1' not only indicates the stability of the complex, but includes the term which is competitive with (and appreciably so at lower pH) complex formation, whereas log K_1 is proportional to the free energy change for the reaction M+L=ML.

In the absorption spectra studies of 1 : 1 complex, with SA as the reference ligand, the following substitution effects can be noted.

Hypsochromic shift : $-NO_2, -SO_3H$

Bathochromic shift : $-CH_3, -Hg, -Cl$

Similar observations were made by Ackerman and Hesse[20] in the case of Fe(III)-phenol complexes. However, the extent of the effect decreases with the increasing number of substituents. For example, the substitution of methyl group in *meta* position shifts the λ_{max} of Fe(III)-phenol complex[20] by 15 nm, while in the case of Fe(III)-SA complex it is only 4 nm.

Since the electron acceptor groups shift the λ_{max} to shorter wavelengths and electron donating groups to longer wavelengths, an apparent correlation between λ_{max} and stability constant is expected. Table 1 also shows that $\Delta\lambda$ and Δlog K_1 values have the same sign. But in the case of Fe(III)-phenol complexes the stability has been regarded as the function of the electron density of phenolate oxygen while the λ_{max} depends on the difference in energy between anion and radical[20]. Similar may be the case with Fe(III)-salicylates and hence any exact correlation between λ_{max} and stability constant is unlikely. This is obvious from the fact that CH_3 group acts as the strongest donor at *ortho* position while considering the pK_2^H and log K_1 values but the λ_{max} of Fe(III)-pCA complex is more than that of Fe(III)-oCA complex Further the λ_{max} of Fe(III)-SA complex and Fe(III)-SoCA complex is the same but their stability constants differ considerably.

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Computations of Apparent Formation Constants and Free Metal Ions in EGTA or EDTA Buffer Systems. Part—I : Effects of *p*H and Metal Concentration with Respect to Ligand

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Thermodynamic formation constants, (log K) (Bjerrum, Schwarzenbach and Sillen, 1957) for each of four hydrogen and metal bound with ethylene glycol-*bis* (β-amino ethyl ether) N,N'-tetra-acetic acid (EGTA) or metal bound with ethylenediamine tetra-acetic acid (EDTA) were used to compute the following apparent formation constants: $K'_{M \cdot HEGTA}$, $K'_{M \cdot HEDTA}$, $K'_{M \cdot EGTA}$, and $K'_{M \cdot EDTA}$ A computer program was developed to calculate these four apparent formation constants for any metal, given its thermodynamic constants, for the full *p*H range (0 1 to 14.0 at increments of 0 1) A more expanded computer program was developed to calculate, for the same *p*H range and for any given metal : ligand ratio, the free metal concentration in the solution, given the metal's thermodynamic constants. The program was utilized to calculate for Ca, Mn, Mg, etc. the exact amount of free metal ion for the full *p*H range and for metal to ligand ratios ranging from 0.01 to 0.1 at 0 01 intervals, for 0.10 to 0.90 at 0.10 intervals and for 0.90 to 0.99 at 0 01 intervals It was possible to show that the free calcium increased by nearly two-fold when the *p*H increased by one-tenth order magnitude, i.e. 0.1 *p*H unit.

CALCIUM is involved in several physiological processes viz., excitation-contraction coupling, action potential of muscle fibre membrane, regulation of enzyme action, etc[1-4]. Highly selective calcium chelating agents e.g. ethylene glycol *bis* (β-amino ethyl ether) N-N'-tetra acetic acid (EGTA) or ethylenediaminetetraacetic acid (EDTA) are frequently used to regulate free calcium ion concentration in the reaction medium. To determine the calcium ion concentration accurately, the applications of exact conditional or apparent formation constants denoted by log K' between the metal ion and the ligand are essential because the value of log K' appears to change as a function of *p*H. These apparent formation constants are derived from a true or thermodynamic value which, for some metal ions, have been already determined by a number of different methods viz., radioactive tracer[6], chelex partitions[6,7] murexides[8], arsenazo III[8], membrane electrode[9] and more commonly by the *p*H titrations[10]. However, the use of selective membrane electrode is not very uncommon and this is carried out in the presence of varieties of buffer, e.g. imidazole, *tris*-maleate, phosphate, etc. The value of the true formation constant as determined by the later method agrees reasonably well with that of *p*H titration value as previously determined by Bjerrum *et al*[10].

The apparent formation constants ($K'_{Ca \cdot HEGTA}$, $K'_{Ca \cdot EGTA}$) are shown to be dependent on *p*H[11-13]. For greater accuracy, both these constants have simultaneously been used to calculate the free calcium ions in this buffer system. Similar calculations were carried out with the EDTA system as well

In the present investigation, the various formation constants, e.g. $K'_{Ca \cdot EGTA}$, $K'_{Ca \cdot HEGTA}$, $K'_{Ca \cdot EDTA}$ and $K'_{Ca \cdot HEDTA}$ have been calculated for the full *p*H range at 0 1 *p*H increments and used in computing the amount of free calcium ion concentration in solution of EGTA or EDTA buffer system.

A computer program was developed to calculate free metal ion concentration in a solution at varying *p*H increments (0.1 to 14.0 at 0.1) and for a given range of metal to ligand ratio. The listing of the source statements of the computer program is presented and the program was coded in Fortran and may be run on most medium to large computers*. The theoretical background used for the program is explained in the next section.

Procedures :

Theoretical background :

The reaction parameters involved in the calculation of free metal ions in Me-EGTA or Me-EDTA buffer system are dealt in two different sections :

(a) Determination of conditional or apparent formation constants ($K'_{M \cdot HEGTA}$, $K'_{M \cdot EGTA}$ $K'_{M \cdot EDTA}$

*Detailed program is available on request.

and $K'_{MeHEDTA}$) from respective thermodynamic constants, which have been determined earlier at known ionic strengths of 0.1 *M* KCl (20°)[1,6,7]. The conditional constants are *p*H-dependent. The EGTA or EDTA ligand is a tetrabasic acid and has four dissociable H ions, being able to associate with the ligand stepwise as shown in the following equations:

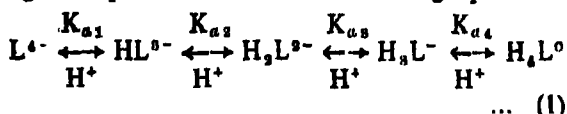
$$L^{4-} \underset{H^+}{\overset{K_{a1}}{\longleftrightarrow}} HL^{3-} \underset{H^+}{\overset{K_{a2}}{\longleftrightarrow}} H_2L^{2-} \underset{H^+}{\overset{K_{a3}}{\longleftrightarrow}} H_3L^- \underset{H^+}{\overset{K_{a4}}{\longleftrightarrow}} H_4L^0 \quad \ldots (1)$$

where L^{4-}, HL^{3-}, H_2L^{2-}, H_3L^- and H_4L^0 are different ionic species, L being the ligand (EGTA or EDTA) and K_{a1}, K_{a2}, K_{a3} and K_{a4} are formation (thermodynamic) constants. The formation constants have been determined under thermodynamic conditions where ionic strength is kept constant in the presence of 0.1 *M* KCl at 20° (see Table 1).

TABLE 1

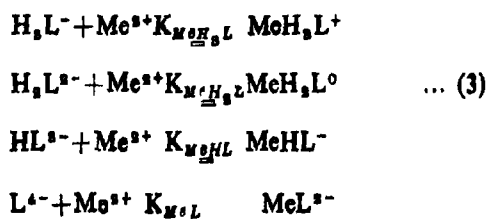
Abbreviation for the constant in the text	Cation	Ligand	Thermodynamic EGTA $\log_{10}K$	EDTA $\log_{10}K$
K_{a1}	H^+	L^{4-}	9.46	10.26
K_{a2}	H^+	HL^{3-}	8.85	6.16
K_{a3}	H^+	H_2L^{2-}	2.68	2.67
K_{a4}	H^+	H_3L^-	~2.00	1.99
K_{MeHL}	Ca^{2+}	HL^{3-}	5.33	3.51
K_{MeL}	Ca^{2+}	L^{4-}	11.00	10.70

From Bjerrum, Schwarzenbach and Silli n (1957).

Applying the law of mass action, the above equation can be presented as follows:

$$[H_4L^0]=K_{a4}\,[H_3L^-]\times[H^+]$$
$$[H_3L^-]=K_{a3}\,[H_2L^{2-}]\times[H^+] \quad \ldots (2)$$
$$[H_2L^{2-}]=K_{a2}\,[HL^{3-}]\times[H^+]$$
$$\text{and} \quad [HL^{3-}]=K_{a1}\,[L^{4-}]\times[H^+]$$

When bivalent metal such as calcium ligands with different ionic species, several calcium complexes are formed. They are shown as follows:

$$H_3L^-+Me^{2+} \overset{K_{MeH_3L}}{\rightleftharpoons} MeH_3L^+$$
$$H_2L^{2-}+Me^{2+} \overset{K_{MeH_2L}}{\rightleftharpoons} MeH_2L^0 \quad \ldots (3)$$
$$HL^{3-}+Me^{2+} \overset{K_{MeHL}}{\rightleftharpoons} MeHL^-$$
$$L^{4-}+Me^{2+} \overset{K_{MeL}}{\rightleftharpoons} MeL^{2-}$$

Hence,

$$[MeH_3L^+]=K_{MeH_3L}\,[H_3L^-]\times[Me^{2+}], \quad \ldots (4)$$
$$[MeH_2L^0]=K_{MeH_2L}\,[H_2L^{2-}]\times[Me^{2+}], \quad \ldots (5)$$
$$[MeHL^-]=K_{MeHL}\,[HL^{3-}]\times[Me^{2+}] \quad \ldots (6)$$
$$\text{and } [MeL^{2-}]=K_{MeL}\,[L^{4-}]\times[Me^{2+}], \quad \ldots (7)$$

where four different types of complexes (MeH_3L^+), (MeH_2L^0), etc. are likely to be formed and each complex will have corresponding formation constants. The last two formation constants are u[sed to] compute conditional formation constant[s] [(see] Table 1), because the charge acquired by the [com]plex is *p*H dependent and the metal-ligand co[mplexes] with a positive charge or with a zero charge ex[ist in] negligible quantities at the physiological *p*H [range]. Therefore, only conditional formation con[stants] (K'_{MeHL} and K'_{MeL}) have been used. (HL^{3-}) and (L^{4-}) are the ionic species [most] prevalent at the physiological *p*H range. These [have] been calculated and will be published elsewhere.

The logarithms of the thermodynamic form[ation] constants for the interaction of EGTA and E[DTA] with H ions and calcium as calculated by Bj[errum] *et al*[10] are given in Table 1.

(b). *Calculation of free calcium ions in the [EGTA] and EDTA systems*:

From equations (6) and (7), we have:

$$K_{MeHL}=[MeHL^-]\,/\,[HL^{3-}]\times[Me^{2+}]$$
$$\text{and } K_{MeL}=[MeL^{2-}]\,/\,[L^{4-}]\times[Me^{2+}]$$

At a given *p*H condition the conditional f[orma]tion constants K'_{MeHL} and K'_{MeL} can be defi[ned as] follows:

$$K'_{MeHL}=[MeHL^-]/[L_{total}]\times[Me^{2+}] \quad \ldots$$
$$\text{and} \quad K'_{MeL}=[MeL^{2-}]/[L_{total}]\times[Me^{2+}], \quad \ldots$$

where $L_{total}=H_4L^0+H_3L^-+H_2L^{2-}+HL^{3-}$[…]

$$\text{Now, } R_1=K_{MeHL}/K'_{MeHL}$$
$$=\frac{[MeHL^-]\times[Me^{2+}]\times[L_{tot}\ldots}{[MeHL^-]\times[Me^{2+}]\times[HL\ldots}$$

(where, K_{MeHL} is a thermodynamic constant [and] K'_{MeHL} is an apparent formation constant).

$$R_1=\frac{[L_{total}]}{[HL^{3-}]}$$

Therefore,

$$R_1=\frac{[H_4L^0]+[H_3L^-]+[H_2L^{2-}]+[HL^{3-}]+[\ldots}{[HL^{3-}]}$$
$$=\frac{[H_4L^0]}{[HL^{3-}]}+\frac{[H_3L^-]}{[HL^{3-}]}+\frac{[H_2L^{2-}]}{[HL^{3-}]}+\frac{[HL^{3-}]}{[HL^{3-}]}+\frac{[L\ldots}{[H\ldots}$$
$$=K_{a2}\,.\,K_{a3}\,.\,K_{a4}\,.\,[H^+]^3+K_{a2}\,.\,K_{a3}\,[H\ldots$$
$$K_{a2}\,[H^+]+1+1/(K_{a1}\,.\,H^+] \quad \ldots$$

Similarily,

$$R_2=K_{MeL}/K'_{MeL}=K_{a1}\,.\,K_{a2}\,.\,K_{a3}\,.\,K_{a4}[H^+]\ldots$$
$$K_{a1}\,.\,K_{a2}\,.\,K_{a3}\,[H^+]^3+K_{a1}\,.\,K_{a2}\,[H^+]^2+$$
$$K_{a1}[H^+]+1 \quad \ldots$$

Since, $Me^{2+}+L_{total}=MeL_{total}$, where $K'_{MeL_{total}}$ is the conditional formation cons[tant], therefore,

$$[K'_{MeHL}+K'_{MeL}]=K'_{MeL_{total}}=\frac{[MeL_{total}\ldots}{[Me^{2+}]\times[L_{t}\ldots} \quad \ldots$$

MeL_{total} is taken as approximately equal to

total cations present and the free ligand, L_{total} as approximately equal to the total ligand minus MeL_{total}.

Equation (14) has been written as a quadratic equation to avoid the necessity of successive calculation of the free metal ions. Hence,

$$Me^{2+}[free] = \frac{-b \pm \sqrt{b^2 + 4K'_{MeL_{total}}[MeL_{total}]}}{2K'_{MeL_{total}}} \quad (15)$$

where, $b = 1 + K'_{MeL_{total}}[L_{total} - MeL_{total}]$

Results and Discussion

The conditional or apparent formation constants for calcium computed as a function of pH, are listed in Appendix II[17].

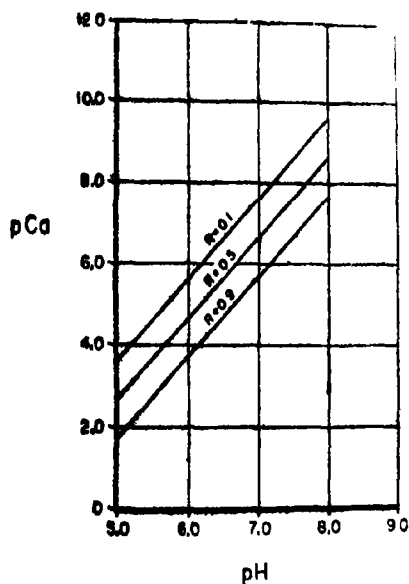



Fig. 1a.

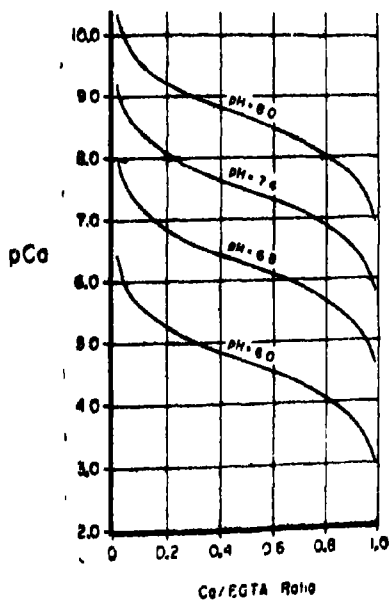



Fig. 1b.

The effects of both pH and the concentration of EGTA on free calcium ions are shown in Figs. 1a and 1b; similar effects with EDTA, another strong chelator of calcium, are shown in Figs. 2a and 2b. Although these studies have been carried out over the full range of pH, in the present graphs only effects are shown between a selected pH range [5.0-8.5], the range over which the pH of the reaction medium could vary physiologically, and at three different ratios of calcium to ligand [Me : EGTA or EDTA, 0.1, 0.5 and 0.9]. Results other than these are listed in Appendix II[17].

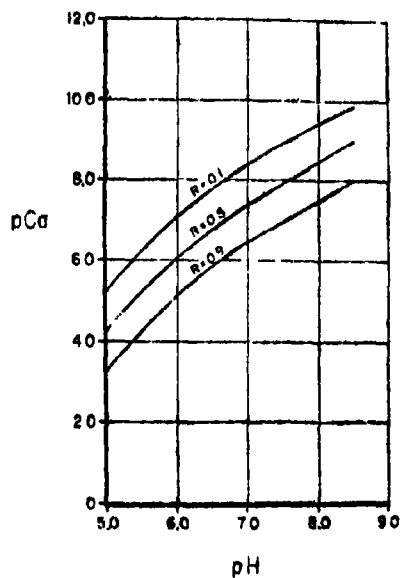



Fig. 2a.

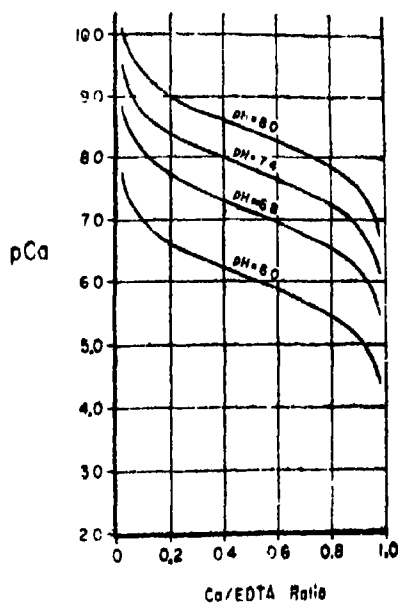



Fig. 2b.

From the Figs. 1a and 2a, it is quite evident that as calcium to ligand ratios increase, the free calcium ion concentration concomitantly increase as shown by the fall in pMe values. When Figs.

1a and 2a are compared as an effect of *p*H, the ligand EDTA seems to behave more effectively as a calcium chelator at least at *p*H 6.0 than at *p*H 8.0 and the effect is quite opposite when EGTA is used. Although, one would prefer to use EGTA over EDTA, when magnesium is also present as a part of the reactant, in addition to the presence of a large quantity of calcium ion; in such situations EGTA is more effectively used as a buffer[14], since the magnesium ions could hardly shift the sigmoidal curves (see Figs. 1a or 2a), thus effecting the free calcium ion concentrations in solution significantly. However, in the presence of equally large amounts of magnesium ions one might expect a shift in the sigmoidal curve significant enough to cause a substantial change in the free calcium ion concentrations. One could replot the curve as an effect of magnesium by successive calculations, alternating with calcium and magnesium until a constant free calcium concentration is obtained. Of course, the prevalence of binding of either calcium or magnesium to the ligand will depend upon their respective formation constants. At least for the EGTA, the formation constants for calcium and magnesium are several magnitudes apart and this makes the EGTA a better buffer to be used when calcium and magnesium are both present in solution.

In EGTA, the effect of *p*H on free *p*Me is linear within a certain range of *p*H (between 5.0 and 8.0) as shown in Fig. 1a. However, in EDTA buffer it is slightly curved within the same *p*H range (see Fig. 2a). The ratio between calcium and ligand does not affect linearity.

Table 2 lists *p*Ca values as computed by the present method, where different values for the formation constants for EGTA were used. These formation constants had been obtained through different techniques using several types of buffers at a constant ionic strength. What is important at this point is to emphasize that the method described by Owen[9] gave the same value of the formation constant [K_{CaEGTA}] to the magnitude of $10^{11.00}$, as previously obtained by the potentiometric titration (Schwarzenbach *et al*, 1957). However, other techniques produced formation constants somewhat lower than those reported in the present table. This change in the formation constant will obviously affect the free *p*Ca in solution. If the *p*Ca values are compared with two different constants, one with $10^{11.00}$ and the other with $10^{10.81}$, a substantial difference in the free calcium ions will be obtained. The difference between these two values could go as high as 50-70%.

Weber and Winicur[16] have used dissociation constant rather than the formation constant to calculate the free calcium in solution (K_{diss} being $1.2 \times 10^{-6} M^{-1}$ at *p*H 6.6). This value was slightly less than what we have calculated with our system i.e., the value at *p*H 6.6 was $1.29 \times 10^{-6} M^{-1}$. This minor difference in the formation constant would lead to a fair amount of free calcium ion difference. It would be safer to use formation constant of the same *p*H, the *p*H at which the reaction is supposed to be carried out. Hence, it was essential to compute the formation constants for each of 0.1 *p*H-unit change. However, the larger the difference as one might conceivably see between the two values of *p*H 6.8 and 7.4, a much larger difference in the free calcium is likely to be obtained.

Owen[9] reported that the formation constant was independent of the buffer solution (e.g. imidazole, *tris*-maleate or phosphate), in agreement with the findings of Schwarzenbach *et al*[15], but he did not agree with the viewpoint of Ogawa[2] and Godt[6], who stated that the formation constant somehow depended upon the type of the buffer used.

The effect of *p*H on the free calcium is quite substantial and this can be ascertained if free calcium ions are calculated at two different *p*H values. For example, at *p*H 7.0, the free calcium ions is in the order of $2.301 \times 10^{-8} M^{-1}$, whereas at *p*H 6.5, a 0.5 *p*H-unit less than the former, the free calcium concentration becomes of the order of

TABLE 2—COMPARISON OF THE FREE *p*Ca AT DIFFERENT K_{CaEGTA} VALUES

Source	Method	KCl (*M*)	Buffer	MgCl ~(m*M*)	ATP (m*M*)	*p*H	K_{CaEGTA} (M^{-1})	$K_{CaHEGTA}$ (M^{-1})	*p*Ca
Schwarzenbach *et al* (1957)	*p*H/potentiometric titration	0.1	Phosphate	–	–	varying	$10^{11.00}$	$10^{5.33}$	7.475
Schwarzenbach *et al* (1957)	*p*H/potentiometric titration	0.1	Phosphate	–	–	varying	$10^{11.00}$	–	
Ebashi (1961)	Radioactive tracer	0.14	10 m*M* *Tris*-maleate	10	–	6.8	$10^{10.81}$	–	6.785
Briggs and Fleishman (1965)	Chelex partition	0.05	30 m*M* Imidazole	4	4	6.7	$10^{10.88}$	–	6.805
Ogawa (1968)	Murexide	0.1	20 m*M* Imidiazole	0 or 10	–	6.8	$10^{10.85}$	–	6.825
Godt (1974)	Chelex partition	0.1 to 0.3	22.2 m*M* Imidazole	5	5	7.0	$10^{10.41}$	–	6.895
Dipolo *et al* (1976)	Arsenazo III	0.1	2mm TES	25	–	7.0	$10^{10.96}$	–	7.435
Owen (1976)	Ca-membrane electrode	–	Imidazole *Tris*-maleate or phosphate				$10^{11.00}$	–	7.475

TES, N-*tris* (hydroxymethyl) methyl-2-aminomethane sulfonic acid.

$2.28 \times 10^{-7} M^{-1}$. At pH 7.5, the value further decreases by an order of magnitude ($2.31 \times 10^{-8} M^{-1}$). Therefore, it is quite conceivable that the application of a more accurate formation constant for the calculation of the free calcium ions is important. Otherwise, a slight difference in the values of the formation constants may add a significant error in the determination of free calcium ions in solution. With a 0.2 pH-unit difference the calcium ions in solution could vary as high as 3 fold. To maintain a required amount of calcium ions in solution for carrying out a specific reaction, the use of Appendix II[17] is recommended to avoid error due to the pH difference.

The added advantage of the present determination is that both the formation constants (K'_{MeHL} and K'_{MeL}) have been simultaneously plugged in the calculation and this will enable the calculation of the free calcium ions to a much greater degree of accuracy. In some instances the effect may not be very large where the pH is low (below pH 7.0), but the effect of the last constant might be pronounced when the pH reaches as high as 8.0 or above.

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Fe(III), Co(III), Cu(II) and Ni(II) Derivatives of Some New Monothio-β-Diketones†

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A few new monothio-β-diketones, [$RCSCH_2COR'$, where R = Ph, Me ; R' = $C_6H_4Cl(p)$, $C_6H_4Br(p)$, $C_6H_4Me(p)$, $C_6H_4OCH_3(p)$] have been synthesized and their metal complexes with Cu(II), Ni(II), Co(III) and Fe(III) were prepared. These were characterized by elemental analysis, ir, magnetic measurements, electronic spectra. Molecular weight determination in refluxing chloroform showed them to be monomeric.

REPLACEMENT of an oxygen by a sulphur atom in β-diketones brings about considerable deviation in the properties of derived transition metal complexes[1,2]. This has led to considerable activity in the field of monothio-β-diketonate derivatives[1-4]. We have synthesized a few new monothio-β-diketones [$RCSCH_2COC_6H_4X(p)$; X=Cl, Br, Me or OMe] having chloro, bromo, methyl and methoxy substituents in the phenyl ring. The present paper deals with a number of their transition metal complexes of Fe(III), Co(III), Ni(II), Cu(II).

Experimental

Diethyl ether (Alembic), methanol (BDH) and acetonitrile (BDH) were dried by the standard methods. Benzonitrile and acetophenones were distilled before use. Sodamide (May and Baker) was used as such. Sulphur was estimated gravimetrically as barium sulphate. Nickel, cobalt, copper and iron were estimated by standard methods[5]. Molecular weight was determined by semimicro Gallenkamp Ebulliometer using thermister sensing in refluxing chloroform. Magnetic measurements were carried out with Gouy's balance at room temperature (308 K). Infrared spectra were recorded in the region 4000-200 cm^{-1} on Perkin-Elmer Model 577 in nujol mulls using cesium iodide window. Electronic spectra were taken on Backman DU-26 spectrophotometer in chloroform.

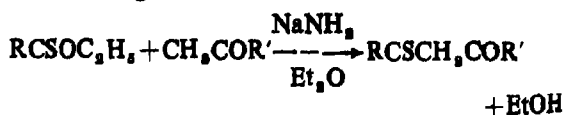
Preparation of monothio-β-diketones[6] : 0.1 mole of substituted acetophenone was added to a stirred etheral suspension of sodamide (0.2 mole) in a three necked round bottom flask (500 ml) fitted with a dropping funnel, mechanical stirrer and a condenser. After half an hour, an etheral solution of ethyl thio ester (0.1 mole) was added dropwise with stirring at 0°. The reaction mixture was then stirred for 3-4 hr and was left overnight. The sodium salt of monothio-β-diketone formed was poured in ice-cold water and extracted with solvent ether. The extract was treated with CO_2 to precipitate the monothio-β-diketones. The solid red to yellow product was filtered, washed with water and then crystallized from ether or ethanol.

Preparation of nickel(II), copper(II) and cobalt(III) monothio-β-diketonate derivatives : A solution of Ni(II) or Cu(II) acetate in aqueous methanol (20 ml) was mixed with aqueous solution of monothio-β-diketone in 1 : 2 molar ratio. The precipitated complex was filtered, washed with water and crystallized from dry methanol or acetonitrile. For the preparation of Co(III) complexes, Co(II) acetate was reacted with the ligand in acetonitrile (Table 2).

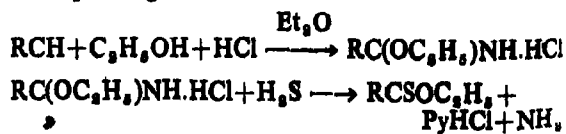
Preparation of iron(III) monothio-β-diketonate derivatives : On addition of aqueous solution of iron(III) chloride to a hot solution of monothio-β-diketones in methanol (1 : 3 molar ratio), a dark brown compound was precipitated which was filtered, washed with water and crystallized from dry methanol (Table 2).

Results and Discussion

The new monothio-β-diketones were prepared by the following route :

$$RCSOC_2H_5 + CH_3COR' \xrightarrow[Et_2O]{NaNH_2} RCSCH_2COR' + EtOH$$

The thione ester can be easily prepared from the corresponding nitrile :

$$RCH + C_2H_5OH + HCl \xrightarrow{Et_2O} RC(OC_2H_5)NH.HCl$$

$$RC(OC_2H_5)NH.HCl + H_2S \longrightarrow RCSOC_2H_5 + PyHCl + NH_3$$

[R=Me or Ph ; R'=$C_6H_4X(p)$;
X=Cl, Br, Me or OMe]

All these ligands were prepared in good yields as red and orange solids (Table 1) and were characterized.

† Dedicated to Prof. A. K. Dey on his sixtieth birthday.

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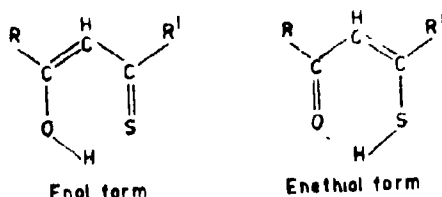
TABLE 1—MONOTHIO-β-DIKETONES, $RCSCH_2COC_6H_4X(p)$ USED IN THE PRESENT WORK

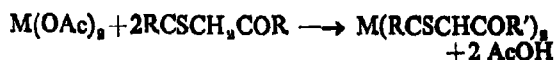
R	X	m.p. (°C)	Yield (%)	S% Found (Calcd.)
Ph	Cl	115	62	11.4 (11.6)
Ph	Br*	129-30	58	9.9 (10.0)
Ph	Me*	124-25	61	12 6 (12 6)
Ph	OMe	121	62	11.8 (11.8)
Me	Cl	38-39	54	15.1 (15 0)
Me	Br	88-89	42	12 4 (12.4)
Me	Me*	67-68	48	16.6 (16 7)
Me	OMe*	56-57	50	15 5 (15 4)

*Reported earlier ; ref. 7.

The ir spectra of these monothio-β-diketones[1-3] display characteristic absorptions in the ranges 1585-1600, 1550-1570 and 1240-1260 cm^{-1} due to $\nu C{=}O$, $\nu C{=}C$ and $\nu C-S$, respectively. In analogy with other thio-β-diketones[1-3], these may exist as an equilibrium mixture of tautomeric enol and enethiol forms which interconvert rapidly by the intramolecular chelate proton transfer[8].

Enol form   Enethiol form

A few latter transition metal complexes of the type $M(RCSCHCOC_6H_4X\text{-}p)_n$, (M=Fe, Co, n=3 ; M=Cu, Ni ; n=2) were synthesized from the corresponding acetate or chloride in methanol or acetonitrile and crystallized from these solvents :

$$M(OAc)_2 + 2RCSCH_2COR \longrightarrow M(RCSCHCOR')_2 + 2\,AcOH$$

$$FeCl_3 + 3RCSCHCOR' \longrightarrow Fe(RCSCHCOR')_3 + 3HCl$$

A similar reaction of cobalt(II) acetate led to the synthesis of the *tris* derivatives only due to the oxidation of cobalt(II) to cobalt(III) in aqueous media by the atmospheric oxygen. All the metal complexes were from dark brown to dark red solids with sharp melting points, soluble in chloroform and benzene. Molecular weight determinations, carried out in a few representative cases showed them to be monomeric in refluxing chloroform (Table 2).

The ir spectral characteristics of the transition metal monothio-β-diketonates were consistent with the conjugated chelate structure, in harmony with the observation of previous workers[1-3]. Of the more significant bands, these metal complexes had two characteristic bands above the 1480 cm^{-1}. The band of higher frequency at 1595-1555 cm^{-1} has been assigned to $\nu C-O$ vibrations, while the band of lower frequency at 1516-1490 cm^{-1} was due to $\nu C-C$ vibration of phenyl ring. The $\nu C-S$ vibration was observed in the region 1235-1255 cm^{-1}. The metal-oxygen and metal-sulphur frequencies could be noted at 440-490 and 345-290 cm^{-1} regions, respectively.

Magnetic susceptibilities of some of the complexes were measured with Gouy's balance (Table 3).

TABLE 2—ANALYTICAL DATA AND PROPERTIES OF THE TRANSITION METALS MONOTHIO-β-DIKETONATE DERIVATIVES

Metal	R	$C_6H_4X\text{-}p$	n	Nature	m.p. (°C)	Metal % Found (Calcd.)	Sulphur % Found (Calcd.)	Mol. Wt. Found (Calcd.)
Ni	Me	CH_3	2	Dark brown solid	216	13 2 (13 3)	14.9 (14.5)	-
Ni	Me	Br	2	Brown solid	224	10.9 (10 3)	11.9 (11 2)	540 (571)
Ni	Ph	OMe	2	Brown solid	208	9 7 (9 8)	10.0 (10.7)	-
Cu	Me	Cl	2	Red brown solid	176	13 3 (13 1)	13.3 (13.2)	460 (487)
Cu	Ph	CH_3	2	Brown solid	193	11.8 (11.15)	11.5 (11 2)	-
Cu	Ph	Br	2	Brown solid	164	9 1 (9 1)	9.6 (9.1)	688 (699)
Cu	Ph	OMe	2	Brown solid	182	10 0 (10.6)	10.8 (10.6)	-
Co	Ph	Br	3	Red brown solid	214	5.5 (5 8)	9 3 (9.5)	1002 (1013)
Co	Ph	Cl	3	Red brown solid	156	6.6 (6.7)	10.8 (10.9)	-
Co	Me	Cl	3	Red solid	164	8.2 (8.5)	13.7 (13 8)	688 (693)
Fe	Ph	Br	3	Dark green solid	178	5.8 (5.5)	9.8 (9.5)	-
Fe	Me	Br	3	Green solid	157	6.2 (6.8)	12.0 (11.7)	-
Fe	Me	Cl	3	Green solid	210	8 3 (8.1)	14.1 (13.9)	692 (690)

TABLE 3—MAGNETIC MOMENTS OF THE METAL COMPLEXES ; M(RCSCHCOR')$_n$

Metal	R	R'	μ_{eff} B.M
Fe(III)	Me	C_6H_4Br-*p*	5 20
Fe(III)	Ph	$C_6H_4OCH_3$-*p*	5 15
Cu(II)	Ph	C_6H_4Cl-*p*	2.08
Cu(II)	Me	C_6H_4Cl-*p*	1.97
Cu(II)	Ph	C_6H_4Br-*p*	1.95
Cu(II)	Ph	$C_6H_4CH_3$-*p*	1.80

The complexes of nickel(II) with these monothio-β-diketones are found to be diamagnetic like other nickel complexes of other monothio-β-diketones[9]. Replacement of one oxygen atom in β-diketone by sulphur causes a change in bond type of the respective nickel(II) complexes from spin free to spin paired. Attempts to prepare cobalt(II) complexes which would be spin paired were unsuccessful. The quick oxidation of cobalt(II) to cobalt(III) also occurs with certain soft bases such as NO_3^-, CN^-, etc[10]. It is of interest to observe that iron(III) complexes with these ligands are spin free like those with other monothio-diketonates. The thio-β-diketonate complexes of copper(II) were found to have magnetic moments of 1.8-2.0 B.M. indicating the presence of one unpaired electron.

Most of the published work on the electronic spectra of metal complexes of monothio-β-diketones has been reported on the nickel(II) chelates. In the case of nickel complexes reported here, the positions and intensity of the bands [630-640 nm (Md – Md) ; 520-530 nm (Md – L_π) ; 405-430 nm (L_π – Md) ; 300-338 nm (L_π – L_π)] are in good agreement with the values of other nickel complexes reported in the literature[9].

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Formation Constants and Thermodynamic Parameters of 2-Amino-3-hydroxypyridine with Some Bivalent Metal Ions

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The proton-ligand stability constants of 2-amino-3-hydroxypyridine (AHP) and formation constants of its chelates with Cd(II), Co(II), Ni(II), Zn(II) and Cu(II) have been determined, using Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti, in aqueous media at different ionic strengths and temperatures. The stability constants of the complexes follow the order Cu(II) > Zn(II) > Ni(II) > Co(II) > Cd(II), which is in accordance with Irving Williams order

Thermodynamic stability constants ($\log K_n^{\mu=0}$) of these metal complexes have been obtained by extrapolating the experimental values to zero ionic strength. The values of overall changes in ΔG°, ΔH° and ΔS° accompanying complexation reactions have also been calculated

THE stability constants of metal complexes with o-aminophenol have been determined[1]. It was of interest to determine the stability constants of corresponding heterocyclic analogue of o-aminophenol, viz., 2-amino-3-hydroxypyridine (AHP). Moreover, survey of literature reveals that no work has been reported on the stability constants of this ligand with bivalent metal ions

In the present investigation, stability constants and thermodynamic parameters of some bivalent metal complexes with AHP have been determined in aqueous media at different ionic strengths and temperatures by potentiometric method.

Materials and methods :

A pure sample of 2-amino-3-hydroxypyridine (AHP) was obtained from Aldrich Chemical Co., USA and its solution was prepared in double distilled water without further purification. Solutions of bivalent metal ions Cu(II), Ni(II) and Co(II) were prepared by dissolving their nitrates while those of Zn(II) and Cd(II) were prepared from corresponding sulphate salts. All the solutions were standardised by gravimetric methods[2]. Potassium nitrate (2 M) was used to maintain the appropriate ionic strengths (0.05 M, 0.10 M, 0.15 M and 0.2 M). KOH solution was prepared by washing KOH pellets with boiling conductivity water and finally dissolving it in CO_2-free conductivity water. It was standardised against oxalic acid potentiometrically. Nitric acid solution was prepared by diluting a calculated amount of the acid with conductivity water and standardisation against KOH solution.

Apparatus :

A digital pH meter (model pH 5651) manufactured by Electronic Corporation of India Limited, Hyderabad, with combination electrode CA-11 (0-14 pH range) was used for pH measurements. The pH meter was standardised with buffer solutions of pH 4.00 and pH 9.20. The temperature was maintained by running water with the help of water circulating pump from a thermostat through a double walled beaker.

Procedure :

The experimental technique of Bjerrum and Calvin[3-4] as modified by Irving and Rossotti[5] was used to determine $\bar{n}$ and pL values.

Three solutions, A : $4\times10^{-3}M$ HNO_3, B : $4\times10^{-3}M$ $HNO_3+3\times10^{-3}M$ ligand, C : $4\times10^{-3}M$ $HNO_3+3\times10^{-3}M$ ligand$+5\times10^{-4}M$ metal (total volume 50 ml in each case), were prepared.

The concentration of the common ingredients were the same in all the cases. An appropriate quantity of KNO_3 (2.0 M) was added to maintain the desired ionic strength.

The mixtures A, B and C were individually titrated against standard KOH solution (0.4 M). The pH measurements were done in an atmosphere of oxygen-free nitrogen at different ionic strengths and temperature. A graph between pH and the volume of alkali added was plotted. The three titration curves so obtained were referred to as (i) acid, (ii) ligand and (iii) complex titration curves, respectively.

Results and Discussion

To calculate the proton-ligand stability constants, the values of $\bar{n}_A$ were calculated at different pH values by noting v' from acid titration curve and v'' from ligand titration curve for the same pH using the following equation :

$$\bar{n}_A=\left\{y T^\circ C_L+\frac{(v'-v'')(N^\circ+E^\circ)}{(V^\circ+v')}\right\}/T^\circ C_L \quad \dots \quad (1)$$

* Author for correspondence.

TABLE 1—PROTONATION CONSTANT OF THE LIGAND AND STEPWISE AND OVERALL METAL-LIGAND STABILITY CONSTANTS AT VARIOUS IONIC STRENGTHS AND TEMPERATUAES

Metal ion	$\log K_n^H / \log K_n$	Temp. 20°					Temp. 30°	Temp. 40°
		$\mu=0.0$	$\mu=0.05$	$\mu=0.1$	$\mu=0.15$	$\mu=0.20$	$\mu=0.10$	$\mu=0.10$
	$\log K_1^H$	–	9.50	9.35	9.24	9.15	9 21	9.07
	$\log K_2^H$	–	6.01	5.89	5.79	5.71	5.74	5.62
	$\log \beta_2^H$	–	15.51	15.24	15 03	14.86	14.95	14.69
Cd^{2+}	$\log K_1$	3.48	3.28	3.19	3.13	3.06	3.12	3 01
	$\log K_2$	3.18	3.04	2 97	2.93	2 89	2 87	2.74
	$\log \beta_2$	6.66	6.32	6.16	6.06	5.95	5.99	5.75
Co^{2+}	$\log K_1$	3.58	3.37	3.26	3 19	3.12	3 16	3 05
	$\log K_2$	3.12	2.92	2 87	2 83	2 79	2.80	2.71
	$\log \beta_2$	6.70	6.29	6.13	6.02	5.91	5.96	5.76
Ni^{2+}	$\log K_1$	3.66	3.44	3.32	3 25	3 18	3.21	3.10
	$\log K_2$	3.04	2 98	2 89	2.84	2.80	2 82	2 75
	$\log \beta_2$	6.70	6.42	6.21	6 09	5.98	6 03	5 85
Zn^{2+}	$\log K_1$	4.36	4.05	3.90	3.80	3 71	3.77	3 64
	$\log K_2$	3.95	3 63	3.48	3.37	3.29	3 36	3.26
	$\log \beta_2$	8 31	7.68	7.38	7.17	7.00	7.13	6 90
Cu^{2+}	$\log K_1$	6.85	6.44	6.23	6.16	5.95	6.02	5.74
	$\log K_2$	5.08	4.57	4.38	4.21	4.02	4.20	4 06
	$\log \beta_2$	11.93	11.01	10.61	10.37	9.97	10.22	9.80

The proton-ligand stability constants were obtained from the formation curves so obtained and refined by various computational techniques[6].

The following equations (2) and (3) were used to calculate the average number of ligands attached per metal ion ($\bar{n}$) and the negative logarithms of the free ligand concentration (pL) at a particular pH.

$$\bar{n}=\frac{(v'''-v'')\,(N^{o}+E^{o})}{(V^{o}+v').\ \bar{n}_A.\ {}^{T^{o}}C_M} \qquad (2)$$

$$pL=\log_{10}\left[\frac{\sum_{n=0}^{n=J}\beta_n^H\left(\frac{1}{\text{anti}\log pH}\right)^n}{T^{o}C_L-\bar{n}\,T^{o}C_M}\times\frac{V^{o}+v'''}{V^{o}}\right] \qquad \ldots (3)$$

The terms used in equations (1), (2) and (3) have their usual meanings.

Metal-ligand formation constants were calculated from the formation curves obtained by plotting $\bar{n}$ against pL. The formation constants thus obtained were refined using various computational techniques[6] viz. (1) correction term method, (2) pointwise calculation method, (3) least squares treatment (simultaneous equations method), and (4) least squares treatment (curve fitting method) and are given in Table 1.

The thermodynamic formation constants were obtained by the extrapolation to zero ionic concentration from the plots of log K versus $\sqrt{\mu}$ and are given in Table 1.

Thermodynamic parameters :

The values of overall change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) accompanying complexation reactions have been determined using the temperature coefficient and Gibbs-Helmholtz[7] equation.

The value of ΔG° was obtained from the expression $\Delta G^{\circ}=-RT\ \ln\beta$ and ΔH° was determined with the help of an isobar equation

$$\frac{d\ln\beta}{dT}=\frac{\Delta H^{\circ}}{RT^{2}}$$

which may be rewritten as

$$\frac{d(\log\beta)}{d(1/T)}=\frac{-\Delta H^{\circ}}{4\ 57}$$

The values of log β obtained at different temperatures were plotted as a function of 1/T. The gradient of the tangent drawn at the point corresponding to 30° was determined and equated to $\frac{-\Delta H^{\circ}}{4.57}$. The value of ΔH° was thus obtained. ΔS° was then evaluated from the relation

$$\Delta S^{\circ}=\frac{\Delta H^{\circ}-\Delta G^{\circ}}{T}$$

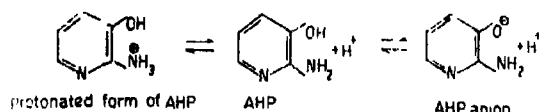
The values of ΔG°, ΔH° and ΔS° are given in Table 2.

TABLE 2—THERMODYNAMIC PARAMETERS OF BIVALENT METAL COMPLEXES WITH AHP
$\mu=0.1M$

Metal ion	$-\Delta G^{\circ}$ kcals mol^{-1} (20°)	$-\Delta H^{\circ}$ kcals mol^{-1}	ΔS° cals $deg^{-1}\ mol^{-1}$ (30°)
Cd^{2+}	8.21	8.39	−0.26
Co^{2+}	8.26	8.39	−0.54
Ni^{2+}	8.41	8.39	−0.096
Zn^{2+}	9.87	9.65	0.86
Cu^{2+}	14.27	14.26	−0.36

In the initial stages of the titration, the ligand curve is shifted to the left (or above) of the acid curve due to the basic properties of the amino group which accepts a proton from the strongly acidic medium.

The protonated species formed dissociates in two steps as shown below :

Protonated form of AHP ⇌ AHP $+H^+$ ⇌ AHP anion $+H^+$

Both 1 : 1 and 1 : 2 complexes could be studied in all the cases. It is evident from Table 1 that log K_1 and log K_2 values at 20° are higher than their values at 30 and 40° with all the metals indicating that low temperature is favourable for complex formation. The stability constants follow the trend $Cu^{2+}>Zn^{2+}>Ni^{2+}>Co^{2+}>Cd^{2+}$ at all the ionic strengths and temperatures. This is in accordance with the Irving Williams[8] order.

All the complexes were found to be enthalpy stabilized. The negative value of $\Delta H°$ in the systems ensure that the reactions are exothermic The entropy factor has been found to be favourable only in the case of Zn^{2+} complex

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Tetravalent Manganese as an Oxidising Agent

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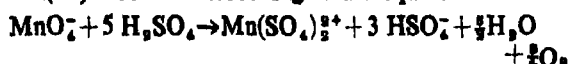
TETRAVALENT manganese in the form of manganese dioxide is known as an oxidising agent for the oxidation of hydrochloric acid to chlorine, Fe(II) to Fe(III) and oxalic acid to carbondioxide and water. MnO_2 by itself does not dissolve easily in sulphuric acid but in the presence of reductants it can be rapidly brought into solution. Stauter and Um[1] in a recent patent suggested the possibility of employing manganese dioxide ores for converting Cr(III) of the chrome ore to Cr(VI). However, there are no reports on the use of Mn(IV) solution as an oxidimetric reagent till recently[2], due to the difficulties in the preparation of a fairly stable solution. During the study of the kinetics of the decomposition of permanganate in sulphuric acid by spectrophotometric methods, Mandal and Sant[3] reported that in 8-11 *M* sulphuric acid, Mn(IV) is formed according to the equation :

$$MnO_4^- + 5\,H_2SO_4 \rightarrow Mn(SO_4)_2^{2+} + 3\,HSO_4^- + \tfrac{5}{2}H_2O + \tfrac{1}{4}O_2$$

The manganese(IV) solution thus formed is reasonably stable, and the change in normality of a 0.1 *N* solution is only 0.1-0.2 percent per day at 25°. Such a solution is a powerful oxidising agent and the standard potential of the redox system $Mn(IV) + 2\,e \rightleftharpoons Mn(II)$ is 1.577 V.

Manganese(IV) sulphate as an oxidimetric reagent :

This reagent has been used for the titrimetric determination of a number of reducing agents. For instance Fe(II), V(IV), U(IV) and Mo(V)[3] are quantitatively oxidised respectively to Fe(III), V(V), U(VI) and Mo(VI) in 1-2 *M* sulphuric acid and titrations can be performed using ferroin as the indicator. Oxalate is oxidised to carbondioxide and water in 1-2 *M* sulphuric acid and titrations with Mn(IV) are possible at 70°. Arsenite is quantitatively oxidised to arsenate by Mn(IV) in hydrochloric acid medium with iodide ion as the catalyst. Mandal[5] reported the use of iodide or iodate as a catalyst, with Mn(IV) colour itself indicating the end point. It has been found by the present authors that with iodine monochloride as a catalyst methyl orange could be used as an indicator.

Manganese(IV) sulphate solution quantitatively oxidises antimony(III) to antimony(V) in the presence of an halogen acid and titrations can be carried out using methyl orange as an indicator Methyl orange is a better indicator than ferroin[6] in a semiaqueous solution containing hydrochloric acid and iodine monochloride. Further, ferroin end points are not reliable due to the fact that ferroin forms insoluble complex with Sb(V)[7]. In sulphuric acid medium and in the absence of chloride, both As(III) and Sb(III) reduce manganese(IV) to manganese(III) and indirect titrations by adding excess manganese(IV) and back titrations with iron(III) show good agreement with those of direct titrations.

Manganese dioxide as an oxidation-decomposition agent :

It has been observed that MnO_2 can be conveniently used as a decomposition agent for the analysis of refractory ores like chromite and sulphide ores like chalcopyrite. Either the synthetically[8] prepared MnO_2 or the naturally occurring manganese ore can be employed for the purpose.

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ERRATA

JICS, LIX, September 1982, pp. 1044-1046

Paper entitled : "Studies in Triethylamine-Water. Part—IV : Predicting the Solubilities of Triethylamine and Water" by S Thangavel and Mathew J Moolel

The figures on page 1045 were not correct The correct figures are as follows.

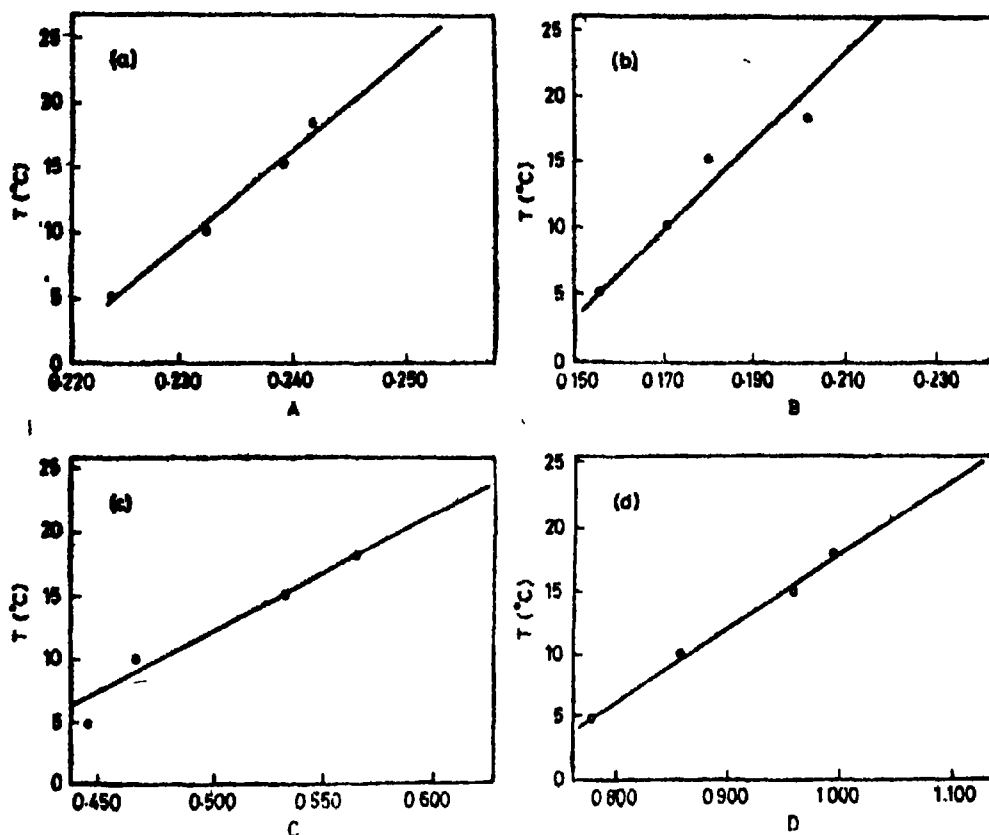



Fig. 1. Variation of the terms A, B, C and D of equation (III) with temperature.

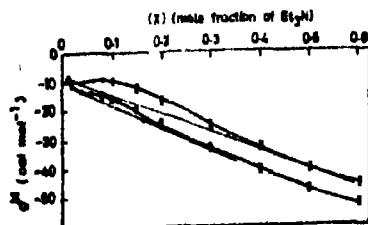



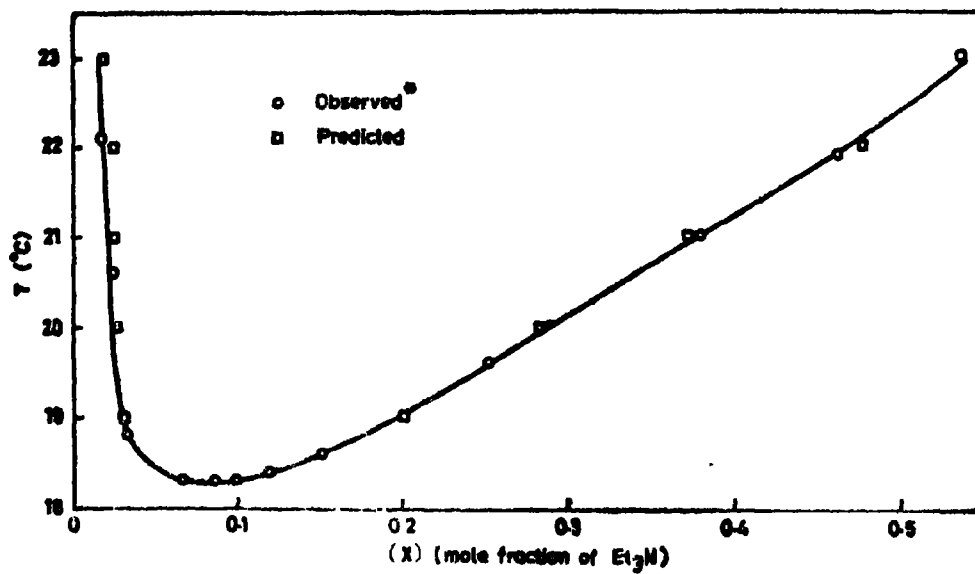
Fig. 2. Variation of g^M with solvent composition (X).

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Fig. 3. Solubility curve of Et_3N-H_2O system.

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